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INTERNATIONAL CONFERENCE «ADVANCED CERAMICS FOR THIRD MILLENNIUM»

Под патронатом Европейского керамического общества

ECERS
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ABSTRACTS

Киев, Украина/Kiev, Ukraine
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CONTENT

TECHNOLOGICAL PRINCIPLES, STRUCTURE AND PHYSICOMECHANICAL PROPERTIES OF CERAMIC NANOCOMPOSITES

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Ceramic nanocomposites are new class of ceramic materials of structural, tool and other functional purposes, which are characterized by heterogeneous structure with average linear size of structure elements less than 100 nm. Four main groups of production processes for ceramic nanocomposites could be marked out:

- mixing nanodisperse powders followed by compaction (pressing and sintering, hot pressing, sintering under high pressure, etc.);
- preliminary synthesis of composite powders with nanostructure of particles by mechanochemical, plasmachemical, colloidal-chemical and other methods, followed by powder compacting;
- reactive sintering of heterophase nanodisperse system, which is accompanied by considerable change in its phase composition;
- synthesis of complex compounds followed by their decomposition in selective chemical reactions (oxidation, reduction, hydride, carbide and nitride formation, etc.).

The main parameters for nanocomposite structure are the morphology and linear size of grains (size distribution of grains), and also the degree of grain and interphase boundary perfectness, including their thickness, purity and fractal dimension. There are these parameters which define the degree of manifestation of size effect essentially depend on choice and optimization of the technology for composite production. In other words, these parameters govern the possibility of achieving the maximum values for mechanical, thermal-physical, electro-physical and other properties of ceramics.

Under large difference in properties of phases in the composite (e.g. conductivity or hardness) it is necessary to additionally account for the special geometrical characteristics of the system as a whole – the extent to which the system is statistical or matrix, the value of the threshold for passing over each of phases, the degree of texturing and coherency of phase. Those parameters of heterophase system are determined to a great extent by the features of technology – relationship between average size of phase particles, homogeneity after mixing, appearing of liquid phase upon sintering, etc.).

The correct choice of the production process for ceramic nanocomposite, the possibility to control the process and its reliability are the indispensable conditions to obtain optimal structure and ensure higher level of its physicomechanical properties compared with single-phase ceramics.

MECHANISMS OF DEFORMATION, FRACTURE AND SINTERING OF COVALENT CRYSTALS IN THE DIFFERENT TEMPERATURE RANGES

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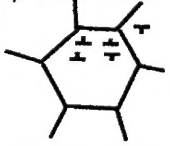
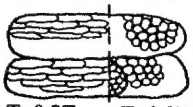
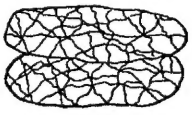
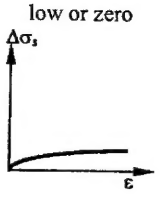
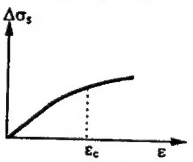
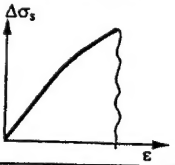
Covalent and partially covalent crystals with directional interatomic bonds are the base for creation of ceramic materials. The concept of characteristic temperature of deformation T* makes possible to classify mechanical behaviour and sintering processes of covalent crystals in different temperature ranges by structural peculiarities. At that three temperature ranges are considered: cold, warm and hot deformation. The boundary between ranges of hot and warm deformation is the recrystallization temperature T_r and the boundary between the ranges of warm and cold deformation is the temperature T*. Structural peculiarities for every temperature range are given in the Table. The pressing of powders may be cold, warm and hot as well. Sintering of powders is possible only at the temperature $T > T^*$, i.e. in the temperature ranges of warm and hot deformation.

Deformation kind	**Hot deformation**	**Warm deformation**	**Cold deformation**
Deformation temperature	$T > T_r$	$T^* < T < T_r$	$T < T^*$
Grain and dislocation structure	equiaxed grain structure, low dislocation density $\rho < 10^6 \div 10^8 cm^{-2}$ 	non-equiaxed grain structure, cellular dislocation structure  $T<0.8T_r$ non-equiaxed cells $T>0.8T_r$ equiaxed cells	non-equiaxed grain structure, random dislocation structure (dislocation forest) $\rho > 10^8 \div 10^{10} cm^{-2}$ 
Strain hardening	low or zero 	grows rapidly with increase of deformation to the ε_c, than grows slowly, $\varepsilon_c \sim \sigma_{ef}^2 \cdot d$ 	grows rapidly and monotonically with the increase of deformation degree to fracture 
Fracture mechanism	ductile	ductile or quasibrittle	brittle or quasibrittle

THE CERAMIC/METAL BRAZED JOINTS: SCIENTIFIC AND TECHNOLOGICAL PROBLEMS, NEW DECISIONS, APPLICATION

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The high temperature nonmetal materials ("ceramics") brazing, soldering, welding are considered. The ceramics of different kinds-based on oxides, carbides, nitrides, carbon substrates, diamond, glasses are included in the consideration.

Among the various joining processes - mechanical, glueing, brazing, welding - two last methods are discussed in details as the more promising.

High wettability and adhesion in ceramic / liquid metal (filler alloy) systems are of key factor in joining processes; complicated problem is the decreasing of the internal stresses in joints as well.

The progress in the high temperature wettability study in experiment and theoretical treatment allow controlling the wetting degree in various practical systems. Physico-chemical processes determined the wettability degree are analyzed. On this bases the principles of creation of filler alloys are proposed.

The decreasing or elimination of a stresses in joints can be reached by various methods: selection of materials to be joined with closed thermals expansion coefficient, use of high plastic filler alloys, by special design of joint, modification of thermal expansion coefficient of metal part at phase transformation, use of gradient materials e.c. These methods are considered.

The manufacture of ceramics-to-metal joining assemblies including the new technological processes is considered.

These assemblies can contain a different nonmetal materials - polycrystal ceramics (oxides, high strength silicon nitride and carbide, aluminium nitride, boron nitride), monocrystals of oxides (sapphire), glasses, graphite, diamond.

A number of these assemblies have extreme properties, particularly strength of joint can rich to 800-900 MPa, working temperatures can be from cryogenic to 300-800 ^{0}C, high optical characteristics can be get for transparent materials (quartz glasses) etc.

The brazing assemblies are used in electronics, optics, space and cryogenics, technics, machinery, tools making.

TOUGHENING OF CERAMICS THROUGH MICROSTRUCTURAL ENGINEERING

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Over the last decade, significant progress has been made in enhancing fracture toughness and reliability of ceramics. By controlling microstructure and composition, high fracture toughness and strength values have been obtained. The key to producing tough and reliable ceramics is the development of elongated grains during sintering or by subsequent thermal treatment which serve to bridge the crack surfaces and impose closure tractions against crack opening. The contribution of crack bridging to toughening depends on the composition of the boundary phase and the aspect ratio of the elongated grains. So far most of the toughening predictions in these systems were based on the measurements of the grain width without reference to grain aspect ratio. In the present paper, a new model is developed which shows that the aspect ratio, rather than grain width, plays an important role in toughening of self-reinforced ceramics. Examples with Al_2O_3, Si_3N_4 and SiC are used to illustrate the validity of the toughening model and to show the potentials of microstructural engineering in developing ceramics with high level of mechanical reliability required in future applications.

RELATION BETWEEN GRAIN GROWTH AND RELATIVE DENSITY EVOLUTIONS DURING SINTERING OF SMALL PARTICLE CERAMICS

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The sintering of pure small grain powders generally begins by a transfer of matter at the grain interface. In absence of a liquid phase, the preponderant mechanisms are grain boundary diffusion and/or surface diffusion, which are both very sensitive to surface segregation. The behaviour of tin dioxide is an illustration of the importance of segregation. It does not densify when pure, but a very fast shrinkage is observed in presence of a very small amount of an additive concentrated on the grain interfaces. The relative contributions of surface diffusion and grain boundary diffusion are then controlled by the additive interface concentration.
For high specific surface area powder such as typical SnO_2 powders, it has been shown that the first matter transfer during heating, which corresponds to surface diffusion, favours grain growth and then an increase of surface additive concentration. When a critical concentration is reached, grain boundary diffusion becomes preponderant and shrinkage occurs. During the complete densification process, relative density (ρ) and average grain size (D) evolve simultaneously: The relation observed is:

$$(1/D - 1/D_0) = B.(1/\rho - 1/\rho_0),$$

where D_0 and ρ_0 are respectively the average grain size and the relative density at the beginning of the densification process. Such a relation can be used to describe the microstructural evolution of several materials (Al_2O_3, with MgO, Y_2O_3 with TiO_2, UO_2 with TiO_2, SnO_2 with MnO_2 or Fe_2O_3), until the moment when abnormal grain growth occurs.

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CRYSTAL GROWTH IN APATITE-MULLITE GLASS-CERAMICS

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A series of six glasses with the generic composition $1.5(5\text{-}x)SiO_2 \bullet (5\text{-}x)Al_2O_3 \bullet 1.5P_2O_5 \bullet (5\text{-}x)CaO \bullet xCaF_2$ were made which could be heat treated to make glass ceramics [1]. The amount of fluorite in the glasses was varied to investigate the crystallisation behaviour and microstructural development in the glass-ceramics as a function temperature.

Glasses were characterised using differential scanning calorimetry (DSC), X-ray diffraction (XRD), Simultaneous Thermal Analysis (STA) and Scanning Electron Microscopy (SEM).

Glasses with high fluorite contents were found to crystallise readily to fluorapatite $[Ca_5(PO_4)_3F]$ via a homogeneous nucleation route probably involving prior amorphous phase separation and so these materials have the potential to be used as castable glass-ceramics for biological applications [2].

XRD analysis showed that fluorapatite and mullite are the main phases present in glasses with high fluorine content and that as the fluorine content is reduced, tendency to anorthite formation increased, particularly at the surface of the monolithic samples tested.

SEM revealed spherulitic structures comprised of discrete acicular apatite crystals that have been hitherto unseen in materials of this type for glasses with an intermediate fluorite content (x=1.5,1.25,1) while glasses with high fluorite content (x=2,1.75) tended to have small spherical crystals indicative of an amorphous phase separation process. An interdependence between the formation of 1) apatite and mullite and 2) mullite and anorthite is postulated and this explains the observed spherulitic patterns.

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FABRICATION AND CHARACTERISTICS OF LIQUID PHASE SINTERED SILICON CARBIDE

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Silicon carbide is difficult to densify without additives, because of the covalent nature of Si-C bonding and low self-diffusion coefficient. The main densification routes for silicon carbide ceramics are: - solid state sintering resulting in materials with very good properties at high temperature, but generally limited strength (< 500 MPa) and toughness (2-4 $MPa*m^{1/2}$); - liquid phase sintering with the aid of metal oxides as Al_2O_3 and Y_2O_3 resulting in nearly fully dense materials with very good room temperature properties but low mechanical performance at T > 1200°C. The main limits of liquid phase sintered SiC are the low fracture toughness and low HT strength.

In this work, dense SiC based materials were produced with alumina and yttria as sintering aids in various percentages, through hot pressing at T=1870°C and P=30 MPa. Annealing treatments were carried out at different temperatures and holding times to evaluate the possibility of a further improvement of the material performance, above all toughness and high temperature strength. The mechanical properties of the annealed materials were related to the microstructural changes and compared to those of the as-hot pressed SiC.

Hot pressed materials have a regular microstructure with equiaxial grains (about 0.5μm grain size) surrounded by Y-Al-silicatic intergranular phase.

The thermal treatments carried out were found to be highly beneficial for improving most properties. Some microstructural changes were observed: i) SiC grain coarsening via both solution-repricipitation mechanism and coalescence with the aid of the liquid phase, ii) formation of plate-like grains; iii) evaporation of grain boundary amorphous and crystalline phases

The best annealing conditions for a substantial microstructure modification without creation of pores and defects were at T=1900°C for 2-4 hours. In the annealed materials, the fracture toughness increased from 3 to 5.5 $MPa*m^{1/2}$, the Vickers hardness from 22 to 25 Gpa. The Young modulus was enhanced in all the materials with values up to 430 GPa and the flexural strength values at 1000°C were almost 20% higher than in as hot pressed samples.

The main factors affecting such improvements are the microstructural changes induced by the thermal treatments, particularly regarding the grain boundary phase, i.e. its reductionand/or elimination.

Si_3N_4-CERAMICS - MICROSTRUCTURAL DESIGN, PROPERTIES AND APPLICATIONS

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The increasing application of silicon nitride materials in different areas makes the tailoring of the microstructure necessary. The possibility of tailoring of the microstructure and properties of silicon nitride materials by using different powders, sintering cycles and sintering additives will be explained. The influence of the microstructure on properties such as strength, fracture toughness, wear and corrosion resistance will be shown. An outlook of future development and application of Silicon nitride materials will be given.

PARTICULATE COMPOSITES WITH THE TETRAGONAL ZIRCONIA POLYCRYSTALLINE MATRIX

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Tetragonal zirconia polycrystals (TZP) show high fracture toughness and strength. This is due to the martensitic transformation of the tetragonal symmetry modification of zirconia grains to their monoclinic form. The transformation occurs at the tip of the crack advancing through the material. It leads to the strain energy consumption which otherwise would be available for crack propagation.

Relatively low fracture toughness of these materials limits their potential applications. Essential improvement of hardness, fracture toughness and wear resistance can be achieved by incorporating into the TZP matrix hard carbide inclusions. The inclusions provoke additional toughening mechanisms. The following of them were identified: crack deflection, bridging and branching. The aim of the present study is to show the effect of the following inclusions: WC, TiC, (Ti,W)C, SiC, Cr_xC_y, NbC, TaC, HfC, ZrC and also Cr_2O_3. Influence of these additives on hardness, fracture toughness and elastic properties of the hot-pressed and pressureless sintered materials will be shown. Interrelation between microstructure of the materials, studied by the SEM and TEM technique, and their properties will be shown.

HIGH PRESSURE-HIGH TEMPERATURE EFFECT ON THE STRUCTURE FORMATION AND PROPERTIES OF HTSC CERAMICS

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We have investigated the peculiarities of structure formation, superconductive and mechanical characteristic variations of melt-textured $MeBa_2Cu_3O_{7-\delta}$-based (Me=Y, Nd, (Y,Nd), Sm) high-temperature superconductors (MT-MeBCO) with and without Ag additions as a function of pressure (2-5 GPa), temperature (750-1500 °C) and holding time (10-30 min).

The high pressure-high temperature treatment enables us for a short time to manufacture practically nonporous MT-MeBCO (the density has been increased by 6-15% up to near 99% of the theoretical one) with improved critical current densities (j_c), microhardness and fracture toughness.

The critical current density of MT-YBCO with an addition of 14% Ag was increased from 11 up to 18 kA/cm^2 (at 77K, self-field, H||c) under the action of high pressure - high temperature. For all the materials under study, the anisotropy of j_c has been decreased due to the increase in j_c in the direction perpendicular to the *ab* plane of $MeBa_2Cu_3O_{7-\delta}$ (H||ab, at 77 K, self-field). The TEM studies have given grounds to suggest that the fact might be associated with an increase in dislocation density in the *ab* plane by four orders of magnitude. The dislocations can serve as pinning centers for magnetic flux lines. The increase in the critical current density might be also attributable to the densification of material.

For all the materials being studied, essential increases in microhardness (by 30%, on average) and fracture toughness have been observed.

The available equipment (the high-pressure apparatuses) makes it possible to treat samples up to 30-35 mm in diameter and 17-25 mm in height.

MICROSTRUCTURE LAYERS OF GRADED COMPOSITE MATERIAL IN FORMULATION SI3N4-TAN-BN DEPENDING ON SINTERING ATMOSPHERE

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The need for improvement in the mechanical reliability and resistivity of two-phase electroconductive composites based on oxygen-free ceramics it asks for development of microstructure approach and improving of the process using to prepare the mixture, optimization the sintering operation. The dielectrical and resistive composites from the systems Si_3N_4 - BN-TaN have been the main focus of our investigations. The thermal linear coefficient of TaN is very close to that of silicon nitride what excludes in advance any thermal mismatch between both of them in ceramic composites used at high temperatures. TaN is also characterized by a higher oxidation resistance than TiN.

Dense Si_3N_4 - TaN composites with the TaN phase in the range of 5 - 50 vol.% were produced by hot pressing technique in the reducing (CO) and neutral (N_2) atmosphere. Two types of ceramic items in the form of the three dimensional component and the functionally graded material were evaluated. The influence of densification parameters, amount and grain size of TaN particles and geometry of the functional zone on the microstructure, mechanical properties and electrical resistivity was investigated. It was proved that the resistivity of electroconductive ceramics is strongly affected by the amount and morphology of the filling phase and is faintly affected by the filling phase's formula. An evident influence of the grain size distribution of TaN powders and morphology of particles of the conductive phase on some electrical and mechanical properties was ascertained. A small quantity of BN powder was added to the starting composition for stabilization of the porosity level in the manufactured composites which essential for the production of reproducible electroconductive composites with positive temperature coefficient of resistivity.

25 YEARS OF EXPERIENCE OF AN EMPLOYMENT OF CORUNDUM IMPLANTS IN THE SURGERY OF SPINAL COLUMN AND JOINTS

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In the open joint-stock company "Ukrainian research institute of refractories named after A.S. Berezhnoy" the manufacture technology of ultradense, porous and variably dense lamellar ceramics more that 99,5 % of alumina was developed.

Experimentally — clinical research carried out since 1976 by the Institute of pathology of spinal column and joints named after professor M.I. Sitenko showed that it is possible and advisable to use this ceramics as endoprosthetic appliances for an implantation in the human body at the surgical intervention in a number of diseases of locomotor system. Such ceramics is biologically compatible with a man organism, lends itself to all types of sterilization, non toxic, does not cause changes of central nerve system functions, does not possess cancerogenic, mutagen and other types of remote action, excludes AIDS infection. When using lamellar ceramics an availability of dense and porous layers allows imitating human bone in maximum approximation. Owing to the biological compatibility and an ingrowths of bone tissue fibers in pores of ceramics the bone-ceramic block is produced which preserves physico-chemical properties of the material during of its long stay in biological tissues.

Rational designs of implants and their manufacture technologies in the Ukrainian research institute of refractories as well as implantation technologies of them in human body are developed. A set of endoprosthetic appliances from ultradense corundum ceramics for the medical treatment of diseases and injuries of spinal column as well as a set of implants from porous ceramics for the substitution of bone defects was developed and is produced now.

25 years of experience of ceramics use in the surgery of spinal column showed that this material as dense and porous implants is in line with requirements of stabilizing and substitutive surgery of loco motor system. The indications for using one or another type of ceramics, surgical interventions technique and tactics of patient observing after a surgical intervention were developed. Good results of medical treatment of patients were obtained in an overwhelming majority of cases.

THE STATE OF THE UKRAINIAN CERAMIC MACHINERY MARKET AND CAPABILITIES OF KERAMMASH TO SATISFY ITS NEEDS

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1. Ceramics is the third industrial material.
2. The state of the Ukrainian ceramic machinery market.
3. Capabilities of JSC Kerammash to satisfy the needs for machinery for ceramic manufacturers.

A. Manufacturing of the special technological equipment:

- equipment which replaces previously imported machinery (membrane pumps, filter presses, vacuum presses, ball mills, vibration sieves etc);
- equipment for shape formation of ceramic tiles;
- equipment for producing semi-finished ceramic tubes, beads, catalyzer bearers and other ceramic items;
- equipment for porcelain insulators production including equipment for diamond finishing of porcelain insulators.

B. Design, manufacture, supply and technical assistance of the production-lines for:

- ceramic tableware;
- roof tiles
- vases
- electric insulators;
- sanitary ware and other ceramic items.

C. Manufacturing and supply of industrial thermal equipment:

- electric chamber and tunnel kilns;
- gas chamber and tunnel kilns.

RESEARCH of METHODS of PRODUCING "HARD" PIEZOCERAMICS

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The piezoceramics on basis PZT (lead of zirkonium-titanium) is now basic industrial ceramics used for production of the majority of components of electronic instrumentation. On its basis the materials with a various combination of electrophysical properties are developed.

Such variety of properties of PZT ceramics is stipulated by introduction in its structure izovalent and heterovalent of cations. Introduction in perovskite a lattice ABO_3 of PZT-ceramics of the various components, and also the ability of ceramics at firing to lose oxid of lead, results in creation defects in cristal lattice. In strong electrical fields such ceramics works unsufficiently stable.

In the literature | 1 | there are informations that the introduction in cristal lattice of an ion of a fluorine instead of oxygen vacancies considerably improves its possibilities to work in strong electrical fields. The authors of this articl such ceramics receive by a method co- precipitation of of a metalo-organic gradients included in its compositions This method has a number of defects: 1 high cost of the initial reagents, 2.toxic liquid wastes.. The data, available in the literature, on influence of the additions are rather contradictory | 2 |, with an explanation of this phenomenon there is some more vagueness.

In this paper we report about influence of the fluoride ion on the piezoelectric properties of a PZT ceramics producing by "dry" process. Obtained by such way, piezoceramic has low significance of a tangent of an angle of dielectric losses and high Q-factor in strong electrical fields. The analysis of the literary data on methods of preparation "hard" piezoceramic is conducted and the attempts of their generalization are made.

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SCIENTIFIC-PRACTICAL RESULTS OF THE DEVELOPMENT OF PRESSED MATERIALS AND ARTICLES BASED ON SILICON NITRIDE

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The development of silicon nitride materials by a hot-pressing method have been conducted at the enterprise for more than 30 years. The unique equipment is the basic achievement in technology. The distinguishing feature of plants is the performing of a pressing process in a vacuum chamber in inert atmosphere at temperatures up to 2000°C and the possibility of squeezing the products at high temperature without disassembly of vacuum system.

The silicon nitride powders with a wide range of granulometric composition which differ greatly from each other in chemical and phase composition are being efficiently applied in the technology. Both ultradispersed powder compositions produced by the plasma chemical synthesis method and coarser silicon powders produced by the self-propagating high temperature synthesis method are being used.

5 marks of materials with unique and varied properties for high temperature (1500°C) and moderate temperature (1000°C) applications have been developed on their basis.

The results of the investigations on development of advanced composite materials reinforced with silicon carbide and silicon nitride whiskers and carbon fibers are presented.

Using the developed materials as the base, the technology for the production of more than 40 advanced articles for different industries has been evolved. A combined approach in the materials development and provision of capacity for work of articles determined the interrelation "material-structure-properties-calculation-design-testing". The materials are widely approbated in heat-, wear- and corrosion - resistant articles.

FUNCTIONAL CERAMICS ON THE BASIS OF PRIMORSKY BASALTS

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The mining industry of Prymorsky region has got maintenance stability problem of technological equipment. This equipment is subjected to the action of abrasive and aggressive environment, that resulted to quick wear metallical details and parts. The problem of both machinery and fire resistance increase can be solved by making use of the local raw materials. The basalts of Shkotovskoe and Sviaginskoe deposits can find application in the Prymorsky region. Basalt is a basis for producing stone casting. The products from stone casting possess some important properties: high abrasive and chemical resistance, mechanical strength, good thermostability, water resistance. Thanks to specific mechanical and chemical properties this products offer resistance to the action of aggressive and abrasive environment. That is why they are an irreplaceable material for protection of equipment in all branches of an industry. The company «BOR» makes use of Prymorsky basalts for stone casting products production – the liners of equipment, the part of which are subjected to the affection of abrasive and aggressive environment. In our days the experiments dealing with producing coating from basalts of Primorye are being carried on. There is a experience of producing such coatings in Primorye. For example in a company "Dalzavod", specializing in repairing ships, the process of repairing steam-boiler was considerably simplified. As a result the maintenance such steam-boiler with basalt coating increased twice. Due to such coating of the inner side of the ladle, giving the melted metal, the number of meltings raised 3 or 4 times. The using of technology of enamel production for receiving protecting coatings was offered by FESTU. The technological improvement of this method is in progress. There are two methods of producing such coating: 1) wet method; 2) dry method. Industrial trials are being carried out.

POLYOMPONENT FIBRES AND CERAMICS BASED ON THEM

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Inorganic fibres may be used as a filler of composites and also as initial materials to produce ceramics. Information about formation of high-temperature fibres and their structural transitions is necessary to regulate the technology of composite materials and to predict their properties.

The aim of the present work was to investigate the mechanism of forming polycomponent fibres $Al_2O_3 - ZrO_2 - MgO$ with different oxide ratios, and also it was our task to find a correlation between a composition, heat treatment temperature of fibres and crystal structure, and properties of ceramics. Study of the process of producing fibrous oxides is of scientific interest from the standpoint of a possible preparation of nanoxide grains uniformly distributed in long objects and of practical interest for production of a component of high-temperature composites and ceramics.

Initial materials were hydrated cellulose fibres and tissues impregnated with mixed solutions of aluminium, zirconium and magnesium salts with a variable ratio: (87,5-98,5) : (1-10) : (0.5-2.5) mol. % in terms of MeO. Polymer salt-containing fibres were thermally treated within a special regime from 100 to 1600^0C. The ceramics were prepared from fibrous $Al_2O_3 - ZrO_2 - MgO$ powders using classic ceramic technology.

For crystal and porous structures to be studied, the X-ray methods, IR spectroscopy, the BET method were adopted. Morphological investigations of a fibre surface were made using a scanning electron microscope.

The conducted investigations made it possible to establish the correlation between amount of aluminium, zirconium, and magnesium oxides in fibres, temperature of their heat treatment and spinel formation, structural changes of aluminium oxide, as well as physicochemical characteristics of fibres and ceramics. The dependence is non-monotonous in nature. The optimum relations between components and temperature ranges of heat treatment are found. These can be obtained by controlling a composition, structure, and properties of ceramic products.

As a result, of polycomponent fibre studies, it was found that over a temperature range of 600-1200^0C the solid tetragonal solution of ZrO_2 - MgO and alumina existed. Above 1200^0C alumina was transformed from θ- and δ- phases to α-corundum. High-dispersion Al_2O_3 interacted with MgO, the solid solution ZrO_2 was partially destroyed. So, the heterogeneous system was arranged and was composed of α-Al_2O_3, monoclinic ZrO_2, tetragonal ZrO_2 and spinel $MgAl_2O_4$, the material integrity was preserved.

SYNTHESIS AND CHARACTERISTICS OF ULTRA-FINE SUPERCONDUCTING POWDERS IN NB-TI-N-C SYSTEM

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Superconducting compounds on a niobium carbonitride base doped with a titanium may be of interest to the technical superconductivity within the helium temperature interval due to their high radiation stability. A solid solution with the optimal composition $Nb_{0.8}Ti_{0.2}N_{0.8}C_{0.2}$ is characterized by the T_c value about 18 K. The critical magnetic field of this material in a bulk state is higher than 17 T, that is not acceptable for the most of technical applications. But it is well known [1] that a size dependent factor is capable to influence essentially on the critical parameters of superconducting materials. Hence a transfer of conventional superconducting materials from a bulk state to a nanocrystalline state may be considered as perspective way for a creation of superconducting high-field materials.

In order to produce desired products with required both dispersion and composition we used a nitrogen plasma of a microwave discharge. The raw materials in these experiments were NbF_5, $TiCl_4$ and propane (in a mixture with butane). A nitrogen and a hydrogen were used as technological gases. We carried out additional cleaning of above listed reagents from an oxygen and aqueous vapor.

The performed experiments have realized a production of monophase powders, which form a continuous series of substitution solid solutions of velvet-black colour with general formula $Nb_{1-x}Ti_xN_{1-y}C_y$ and the NaCl type structure. A full mutual solubility of both Ti and Nb in these phases was noted, but we did not aspire to produce the carbonitride powders in these experiments with a substitution of N to C more than 40%. A powder dispersion of the $Nb_{0.8}Ti_{0.2}N_{1-y}C_y$ powders was increased from 30 to 45 m^2/g at N to C substitution, and of the $Nb_{1-x}Ti_xN_{0.2}C_{0.8}$ powders was increased from 35 to 72 m_2/g at increasing a Ti content in them. The critical magnetic field of the produced ultra-fine carbonitride powders was on the level of 50 T at substituting a niobium by a carbon up to 30 at.%, and then decreased abruptly. The analogous dependence on a titanium content was monotonous with the maximum on the $Nb_{0.8}Ti_{0.2}N_{0.8}C_{0.2}$. Thus, synthesis of Nb-Ti-N-C in form of ultra-fine powders has resulted in producing the perspective high-field superconducting meterial, the critical magnetic field of which is 3 times larger as the known maximum value for traditional materials is.

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NANODISPERSIVE HYDROXYAPATITE POWDER

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The main component of hard tissues of alive organisms is hydroxyapatite (HA). In recent years preparations, based on HA, find wide application as a powder with sizes of particles 0.1-0.5μ and also macroporosity and high density ceramics. However, at liquid phase synthesis of HA a powder with the sizes of particles 1-10μ is received. Though on the initial stage of reaction the sizes of «primary» particles are less then 0.1μ, because of necessity of long stending of a deposit in the certain conditions for «maturing», i.e. the increasing of the relation Ca/P from 1.50 up to 1.67 in it «primary» particles stick together and unite in agglomerates. As the result a substantial growth of particles sizes of the deposit is occured. At drying of a powder even the greater integration of particles is occured. It is practically impossible to make «superthin» crushing of such granulated powders to the sizes of particles equal the sizes of primary microparticles by drying milling. The process of molecular-dense aggregation and coagulate of microparticles interfere such a crushing, that limits a degree dispersion of the powder.

In the given work at a finishing stage of a wet synthesis the «primary» particles were covered with a thin layer of surface - active substance (SAS) for obtain the nanodispersion powder. It resulted in increasing of distance between microparticles and, accordingly, decrease of attraction forces between them and also to weakening of coagulation and coalescence processes. A covering was carried out by loading of suspension in a spherical mill and dispersion it during 6 hours. Dispersion resulted: to disaggregation of the powder to primary microparticles; to formation in a granules disintegration process of new phases separate surfaces in system of the particle - SAS; to increasing of atoms activity on these surfaces; to adsorption of an organic nature SAS on surfaces of microparticles. Extraction of a SAS from a surface of particles made by high-temperature annealing at temperature 750^{O} C.

The SAS treatment of the deposit resulted in decreasing of the average size of particles to 0.2μ. X-ray and IR analyses showed, that was no changes in phasic structure or at a molecular level in the dispersive powder in comparison with a standart one.

SOME REGULARITIES OF SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS OF ALUMINUM NITRIDE

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Nowadays, aluminum nitride is known as a most promising material for the production of ceramic substrates used in electronics due to the combination of high thermal conductivity and electroinsulating properties. The properties of AlN-based ceramics are highly dependent on the properties of the initial aluminum nitride powder.

The present paper demonstrates some regularities of synthesizing aluminum nitride from the green mixture of Al+AlN. The influence of the green mixture composition on combustion temperature, particle morphology, and chemical composition of the aluminum nitride obtained has been studied. The synthesis optimum conditions have been determined.

During our investigations we observed that an increase in the synthesis temperature resulted in enlargement of AlN grains; at T=2350°C the grains were maximum in their size (about 20-30 μm) and edged in their form. Besides, the product partials sintering took place. When the aluminum content in the green mixture was 70%, the combustion temperature exceeded the dissociation temperature of aluminum nitride. Under such terms AlN particles of various shape and size were formed. When the synthesis was carried out at the green mixture combustion limit, the product of synthesis consists of separate particles of submicron size. The specific surface of the AlN obtained ranged from 0.1 to 2.5 m^2/g depending on a synthesis temperature mode. The green mixture composition and, therefore, the synthesis temperature significantly affected the purity of the synthesized aluminum nitride. When the synthesis temperature was close to the dissociation temperature of AlN, we obtained the purest product.

EFFECT OF ALUMINA POWDER QUALITY ON DENSIFICATION OF ALUMINA-BASED CERAMICS

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The quality of raw materials as well as processing way to elaborate a ceramic material are essential for quality of the resulted material. Therefore much work was done to both improve the values of raw material characteristics and diversify or optimize the processing parameters.

For this study three types of alumina powders were used. Distinctly, these powders are characterized by different average dimensions of the particles: 8.50 μm, 2.05 μm, and 0.41 μm, respectively.

With these alumina powders were elaborated different compositions of alumina-based ceramics. The per cent of alumina, as raw material, was from 100 to 94 %. The added powder was steatite. After compaction of the powders the thermal treatment, at different temperatures, was done. The effects of alumina quality as well as of the thermal treatment on the resulted density and structure of the ceramic material is pointed out. The experimental results are discussed.

SYNTHESIS OF CERAMICS BASED ON THE MODIFIED HYDROXYAPATITE

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Compounds having an apatite structure are of strong current interest because they hold promise for technological applications as adsorbent|1|, catalytic agent|2|, luminescent|3|, bio-active|4| etc. materials. In many cases the best results are achieved by including of atoms of other elements, among them rare earth elements, in their structures. The necessity of studying of their replacement limits in apatite stems from that fact. The results of an investigation of the $M^{2+}_{5-2x}M^{+}_{x}M^{3+}_{x}(EO_4)_3OH$ systems, where M^{2+} -alkaline earth , M^{+} - alkaline, M^{3+} - Bi, Y and rare earth elements , E - phosphorus, vanadium are presented. A special feature of the synthesis of hydroxyapatite and its solid solutions is that the resulting products frequently are accompanied by alkaline earth metal orthophosphate. This fact is caused by two reasons: firstly orthophosphate is both a primary product of reaction of hydroxyapatite formation and a product of its thermal decomposition; secondly the chemical compositions of this compounds are extremely close together (the molar ratio M\E are equal 62,5/37,5 and 60/40 accordingly). This generate a need for a careful choice of the synthesis temperature for each concrete case and a rigid requirements to the contents of components in mixtures for synthesis. The synthesis of $M^{2+}_{5-2x}M^{+}_{x}M^{3+x}(PO_4)_3OH$ has been performed by a ceramic technology at final temperature 1100^0C. In some containing Sr systems calcination has been carried out in an water vapor atmosphere . The ranges of solubility in these systems reached up to x = 0,1 - 1,4. The synthesis of $Ca^{2+}_{5-2x}M^{+}_{x}M^{3+}_{x}(VO_4)_3OH$ has been carried out by pyrogenic decomposition of the containing all components tartrate solutions at 450 - 550^0C with following calcination at 700^0C. The solubility is within the concentration range up to x = 0,05 - 0,45. The examination of the obtained data has shown, that the sizes of three-charge cations are the controlling factors for the limits of solubility and the cell parameters , all other factors being equal. It has been established by an IR spectroscopy and NMR. that the $Ca^{2+} \rightarrow M^{+} + M^{3+}$ substitution have a dramatic influence on a state of OH^- ions, as evidenced by the reduction in intensity of the IR spectra bands associated with the stretching and libration modes of OH^-.

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SYNTHESIS OF CATALYTIC COVERAGES ON HIGH POROUS CELLULAR MATERIALS

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The catalytic purification methods removing and exhaust fluids from parasitic compounds in power engineering, chemical industry, motor-vehicle transport are the most effective. High porosity cellular materials (HPCM), having properties, valuable to the carrier - high porosity and permeability, are by perspective carriers of catalytic compositions. The manufacture HPCM is possible on the basis of ceramics, and also metals and their alloys.

The gases purification processes are economically expedient by using catalysts not keeping precious metals. The most catalyticly active oxides are the composite oxides such as perovskite-type. The main performances, defining their catalytic properties, are a chemical composition, condition of production. The technological parameters of catalytic synthesis coverages from a nickel titanate and lanthanum cobaltate on HPCM from a nichrom X25, cordierite are studied in work. The high activity of selected compounds is determined by d-metals presence. The method of a deposition perovskite-type of as $NiTiO_3$ on a HPCM–Ni-Cr/ γ-Al_2O_3 (12 wt.%) and HPCM-cordierite is tested. A deposition realized from solution of salt $NiSO_4 \cdot 7H_2O$, into which one was brought TiO_2. The solution NaOH as the precipitant have used an amount of the precipitant determined by stoichiometry. The deposition time varied from 3 till 12 hours. The heat treatment conducted at 900-1150 °C. X-ray for model HPCM –Ni-Cr/γ-Al_2O_3, with deposited reactants, after heat treatment at 1000-1200 °C has shown availability initial anatase, actuations of a nickel, chrome oxide without reflex $NiTiO_3$. As a result of synthesis $NiTiO_3$ on HPCM from cordierite «clean» perovskite is obtained already at 1000 °C. The specific surface $NiTiO_3$ makes 1,5-2,0 $м^2/g$. A deposition lanthanum cobaltate is realized from solution of a lanthanum nitrate with Co_3O_4 by solution NaOH. The powders are synthesized at 600, 700, 800, 900, 1000 °C with exposure 2 hours. X-ray has installed formation lanthanum cobaltate already at 600 °C with tracks La_2O_3, cobalt, after 800 °C - $LaCoO_3$ and La_2O_3, after 1000 °C - $LaCoO_3$.

Thus, as a result of the conducted researches the catalytic coverages such as perovskite-type are obtained. They can exchange noble metals and reduce the cost of catalysts future.

SYNTHESIS OF HIGHDISPERSION POWDERS ON A BASIS OF OXYGEN-CONTAINING COMPOUNDS

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Calcium hydroxyapatite $Ca_5 (PO_4)_3OH$ is widely used in various branches of a science and engineering. One of perspective directions is its application in medicine as ceramic products replacing bones at orthopedic operations. However, application of such ceramics is limited, because of its insufficient mechanical durability, which depends on many factors, major of which are dispersion of an initial material and presence plastificators. The structure vanadate apatite is similar to structure phosphoric one ($Ca_5 (VO_4)_3OH$). The items of information on its using as a laser material have appeared only last years. It is considered, that more effective for such purposes are the compounds, which structure of cationic sublattice includes some various metals. For manufacturing qualitative ceramics it is required high dispersion and homogeneity of an initial material, and also the least temperature of synthesis. Traditional methods of synthesis (the ceramic technology and precipitation from solutions) does not allow to receive materials with necessary properties. A method close in the essence to spraying drying was the most acceptable. The reception vanadate and phosphoric apatites can be shared into two stages. At the first stage it was created solutions, which composition included all required components in the strictly given ratios. For preparation of such solutions were picked up necessary complex formers and the values pH are determined. Besides into solutions it was entered components, which at thermal decomposition were used as looseners. At the second stage the prepared solutions by dose it was entered into the furnace, heating up to optimum temperature. By development of methods the special attention gave to the control of a gas atmosphere in a zone of reaction. The developed methods have allowed to synthesize vanadate and phosphoric apatites as single-phase products at temperatures relatively 650 and 800°C.

At using of the given technique the various materials were received on the basis of phosphoric and vanadate apatite with mutual replacements of anion (vanadate on phosphate) and cation (calcium on others alkaliearth metals or on alkaline and REE metals). The technique was also successful tested at synthesis others complex oxygen contaning compounds with participation of titanium, zirconium, hafnium, antimony, niobium, tantalum, molibdenum, tungsten in the highest degree of oxidation.

ESR INVESTIGATIONS OF ZIRCONIA NANOPOWDERS

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The study of ZrO_2 has attracted considerable attention because of its various important applications. In the past several years, a flourish of activity on research directed toward synthesizing ZrO_2 with nanoscale dimensions has taken place. This paper is concerned with reporting the ESR properties of zirconia nanopowders. The parameters of ESR signals are discussed in terms of the observed particle size effect.

Nanopowders was obtained by a method of coprecipitation. The ultrasonic, microwave irradiation and pulse magnetic field treatment of hydrohides were carried out in order to prepare extremely small crystallite size powder with a narrow size distribution. The ESR measurements were carried out on a PS-100X spectrometer with a TE_{102}-mode double cavity. The spectra were recorded in the X-band at room temperature. A Mn^{2+}/MgO solid solution and/or a magnetic field measuring unit were used to calibrate the magnetic field strength. The magnetic field ramp during data acquisition was controlled by an interface connecting the spectrometer console to a personal computer. The data acquisition parameters used were the following: modulation amplitude 1000 mG, microwave power 8 mW, scan number 10. The nanopowders ZrO_2 were used as a loose power for the ESR measurements.

The characteristics and the results of ESR measurements of all powders calcined at different temperatures are listed in Table 1. X-ray diffraction analysis of these simples showed that all powders are crystalline and contain monoclinic and tetragonal phase. All the samples have ESR signals, composed of two kinds of lines, which are assigned to axially symmetric signal Zr^{3+} at $g_{\perp}$=1.9764 and $g_{\parallel}$=1.9598 and wide line at g≈2.

Calcination temperature, °C	Calcination time, h	Crystallite size, A°	Phase, %	$n_{Zr^{3+}} \cdot 10^{18}$ spin/g	$N_{g=2} \cdot 10^{22}$, spin/g
450	0.5	100	77M+23T	0.9	6.5
500	2	120	96M+4T	5.4	18.4
700	2	180	88M+12T	7.6	23.7

ESR signal about g≈2 belongs to +1/2↔-1/2 transitions of paramagnetic centers in weak crystal field. The bulk Zr^{4+} ions, which are adjacent to the bulk oxygen vacancies, could capture electrons resulting in the formation of Zr^{3+} ion. One can see that a number of paramagnetic center decrease with crystalline size of nanopowders.

NANOSIZE CERAMIC POWDERS BASED ON SIO_2 MODIFIED BY TRANSITION METAL OXIDES

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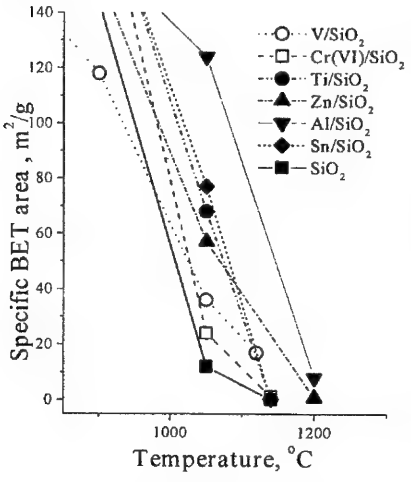
Nanosize ceramic powders have been synthesized by means of modifying the pyrogenic silica (A-300, size of primary particles 5-50 nm) with metal oxides (V, Cr, Zn, Ti, Sn, Al). Gas-phase synthesis has been carried out using volatile chlorides and oxochlorides of the metal and $Zn(Acac)_2$. It was studied the thermal stability of obtained powders, content of metal in which was 1–2,5 %. Specific BET area of powders calcinated at different temperatures in the range 500-1200 °C has been measured. A sharp decrease of a specific BET area of the sample with metaloxide phase was observed at higher temperatures, than for a pure silicon dioxide that indicates the increase of thermal stability of such materials up to 50-100 °C (Fig).



Step by step carrying out modification, hydrolysis and dehydration, powders containing 1-4 layers of metal oxide on the surface have been synthesized (1–10 % in recalculation on metal). By method of scanning electron microscopy it was found that the increase in the content of metal (Cr) from 0.5 up to 5.2 % did not destroy a globular structure of the initial silica. The increase in the content of metal certainly influences their thermal stability. So, for samples, which contained the oxides Cr, Ti and Sn the decrease of thermostability with increase in the content of metal was not observed. The specific surface area of powders calcinated at 1000 °C decreased in an inappreciable extent for Ti- and Sn-, but for Cr-oxide-phase was increased with enlargement of the content of metal in silica matrix. The specific BET area of the samples, which contained Zn and V oxides, decreased with magnification of their content sharply.

SELF-PROPAGATING SYNTHESIS OF LEAD OXIDES IN SYSTEMS $Na_2O_2 - PbX^z_{3-z}$ ($X^z = F^-, Cl^-, Br^-, I^-, SO_4^{2-}$)

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The great attention all over the world now is given to a problem of clearing and deeper processing of the industrial waste. Self-propagating process is perspective because it allows essentially to reduce the power consumption at the production of various substances.

The detected possibility of self-propagating synthesis (SPS) of lead oxides from low-soluble and thermally stable lead salts, at the interaction with Na_2O_2, can be used for processing waste of sulphate, storage and other productions.

By methods of DTA, TG and X-ray phase diffraction analysis it was established, that the interactions can be represented by the general scheme:

$$Na_2O_2 + PbX^z_{3-z} \rightarrow PbO + Na_zX^z + \tfrac{1}{2}O_2,$$

where $X^z = F^-, Cl^-, Br^-, I^-, SO_4^{2-}$.

Rather low temperatures of SPS and obtained oxygen in systems with $PbBr_2$ and PbI_2 result in formation of some share of other lead oxides, thereof the product has not yellow (for $PbSO_4$, PbF_2, $PbCl_2$), but brown (for $PbBr_2$) and dark brown (for PbI_2) colour. The lead oxides free from sodium sulphate and halogens were obtained by washing of the product SPS by water.

Usually observable the velocities of the front SPS (U) are from 25 up to 220 mm/min. The possibility of the realization SPS and its velocity U was determined by components ratio, degree of their dispersion, geometry of a sample, a mode of pressing, heat release of mixtures and kinetic parameters of transformations.

The comparison for all investigated systems of significances U, measured at identical conditions has shown, that the velocity of front SPS strongly depends on thermal stability of initial lead salts and will increase in a row with anions:

$$SO_4^{2-} \approx I^- < Br^- < F^- < Cl^-$$

The processes proceeding in front SPS, can be described by system of the differential equations including the equations of a chemical kinetics and a heat conduction equation with an internal source and losses of heat [1].

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ELECTROCHEMICAL SYNTHESIS OF CHROMIUM, MOLUBDENUM AND TUNGSTEN SILICIDES FROM HALIDE-MELTS

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Thermodynamic analysis and voltammetric measurements showed that HTES of silicides of group VIA metals could only be performed in the kinetic regime. In this case the sequence of the stages is the following: 1) electrodeposition of a more electropositive component (Mo and W in the elemental form, Cr in the form of Cr_2O_3), 2) electrodeposition of the second component silicon on the surface of an oxide or of a metal deposited earlier, 3) reaction diffusion of silicon into the bulk of the metal-salt pear to produce silicide phases varing in composition up to the highest silicides MSi_2.

The HTES of chromium silicides was performed in the system KCl-KF-K_2SiF_6-K_2CrO_4. Both the pure phases of Cr_2O_3, Cr_3Si and $CrSi_2$ and mixtures of these phases with a small content of silicon were obtained, depending on the composition and the electrolysis parameters. In selecting the concentrations of CrO_4^{2-} and SiO_2 (K_2SiF_6) it is necessary to take into account the fact that in the first stage of the electrolysis a Cr_2O_3-salt pear is formed, which begins to get siliconized as high-melting metal is depleted. Contrary to the HTES of Mo and W carbides in this variant of the synthesis one of the components is deposited not in elemental form, but as an oxide, and the other is the reducing agent of this oxide.

The electrosynthesis of molybdenum and tungsten silisides was performed from NaCl-Na_3AlF_6-Na_2MO_4-SiO_2 melt (M-Mo, W). In the first stage of the electrolysis, the metal-salt pear is formed, and the process of silicide electrodeposition begins as the oxy salt of a high-melting metal is depleted.

The temperature and current density are of special significance in HTES. Below 1123 K, the reaction of Mo (W) with Si does not go to completion, while above 1223 K the stability of the metal-salt pear decreases and silicides are nit formed. If the composition of the melt is optimal, the pure binary silicides $MoSi_2$ and WSi_2 are obtained at i_c – 0.5-1.2 for MoSi and 0.5-1.5 A.cm^{-2} for WSi_2. At $i_c < 0.5$ A.cm^{-2} the target product is contaminated with the free metal, while at $i_c > 1{,}2$ A/cm^2 a double silicide phase (Al, Si)$_2$ Mo appears in the molybdate-containing melt. The specific surface area of the powders is 5-15 m^2 g^{-1}, the particle size 0.5-2.0 μm. The yield of $MoSi_2$ 0.2-0.3, WSi_2 0.3-0.45 g (A·h)$^{-1}$.

MICROPOWDERS of Au-NiO

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The metal–ceramic micro- and nanopowders can be applicable in many fields of the modern electronic technologies, such as composite materials, thin and thick films or electrochemical devices (gas sensors, fuel cell electrodes, conductive and resistive paste components, etc.). The physical phenomena correlated with interfaces and interlayer in this material strongly depend on the size of metal and ceramic particles.

In the present work structural investigation results of Au-NiO nano-powders are presented. The powders were prepared from aqueous solution of aurum chloride and nickel(II) nitrate using the ultrasonic spray pyrolysis technique. The aerosol produced by means of 2.6 MHz nebulizer was transported with the stream of reduction gas mixture (Ar + 15 vol%H_2) into reaction tube heated up to 650°C. Then, in the cold reactor zone the Au-NiO particles were gathered with an electrofilter.

The physical properties of obtained powders were next characterized using different methods: microstructure, particle size distribution and local chemical composition by TEM and AFM, specific surface by BET. Additionally, the electrical properties, like DC and AC conductivity were examined.

It was found that the small crystallite form spheres dia. 10÷50 nm. The specific surface of obtained samples was 40÷120 m^2g^{-1}, depending on initial salts concentrations. In the figures a) and b) distribution of Au and Ni particles is presented. It can be stated that both examined metals were uniformly distributed on the sphere surface.

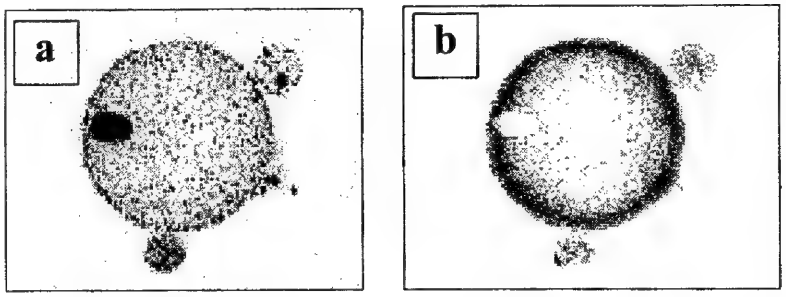

Fig. Surface mapping of the elements (TEM, 100000x): a) gold, b) nickel

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FORMATION OF SURFACE PARTICLES MORPHOLOGY OF METALLIZED Al2O3 BY THERMOSYNTHESIS IN VIBRANT STRATUM

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The plating of ceramic and abrasive powders - electroemery, diatomite, carborundum, carbide of boron etc. different metals allows essentially to improve running characteristics – pressing-, sintering ability - such "«rigid" blends at their processing in hardware products -, hones and circles, metal-abrasive granules (pellets).

Particular advantages there is a method of plating of ceramic powders (thermosynthesis of ceramic-metal composites) at heat treatment on the technology of a vibrant stratum concerning to "«dry" methods of plating and permitting is dosed to plot finely dispersible (1-5 microns) topcoats - copper, nickel, cobalt, wolframium etc., having any link - mechanical, adhesion, chemical - with powder-base [1, 2].

The shaped morphology of particles surface of rendering essential effect on running characteristics of a ceramic-metal powder and subsequent guard ropes of receptions of his further processing, can represent following (see microphoto.):

- separate dot (as spherical and cylindrical like) inclusions uniformly distributed on all surface of particle;
- of spot and extended areas of a porous metal film coating particles surface on 30 -70 %,;
- continuous metal film, reaching to of the shell, sublayer replicating uniformly an outline of particle

Feature of morphology of shaped films is their developed surface, which one can be characterized not only presence alone of stratum, but also presence of thin "whiskers" ~ ø 1 mcm, "rising" perpendicularly of surface and providing heightened autohesion to ceramic-metal powders and their activated sintering.

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SOL-GEL PROCESSES IN TECHNOLOGY OF THE FINE-CRYSTALLINE CERAMIC POWDERS

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The manufacturing of the fine-crystalline oxide powder materials for constructional ceramics was possible at application of sol - gel processes on the fine structures formation at a colloidal level and preservation them in during of physical and chemical transformations "solution - hydrosol - gel - oxide". It was experimentally established that one of the most important reasons of formation and preservation of fine structures is the prevention of sol microparticles aggregation owing to superficial contacts. On an example of zirconium hydroxide it was shown, that a major factor of sol aggregation is the chemical processes of inside- and interparticle olation and oxolation. We established the mechanisms and kinetic characteristics of these processes. For prevention of sol aggregation it was offered to utilize the organic solvents at stages of gelling and dehydration of hydroxides. Organic molecules adsorb on a surface of hydroxides particles and as result prevent interparticle processes of olation and oxolation and also reduce forces of capillary tension at dehydration of a hydroxide deposit. Also they promote destruction of particles formed before agglomerates.

Theoretically and experimentally we confirm conditions of collateral precipitation of zirconium with cations of yttrium, magnesium and aluminium with the purpose of manufacturing of fine-crystalline powders of the stabilized dioxide of zirconium. It was established that the conditions of hydrosols dehydration at a stage of "sol - gel - oxide" are essential for preservation of fine structure of oxide at its heat treatment. On the basis of carried out researches the experimental party of powders of the stabilized zirconium dioxide was prepared. The samples of constructional ceramics has the following indexs: density - 5,98 g/cm^3, flexural strength – 1150 mPa, cracking fissuring - 19,5 mPa/m^2.

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THE INFLUENCE OF MECHANICAL ACTIVATION ON SYNTHESIS OF CORDIERITE

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Cordierite based ceramics is a widely used electronic material due to its promising properties such as low linear thermal expansion coefficient, high resistivity, low dielectric constant and low dielectric losses. There are numerous experimental routes for the synthesis of cordierite. The subject of this work is the obtaining of cordierite using mechanical activation as a process that modifies physical and chemical properties of starting powders. The initial mixtures of basic magnesium carbonate and kaolinite powders were mechanically activated in a high-energy vibro-mill by grinding for 10-40 min. The influence of mechanical activation on the formation of cordierite by reaction sintering was examined by analyzing data obtained using X-ray diffractometer, differential thermal analyser and sensitive dilatometer. It was established that the increase of activation time initiates the formation of cordierite phase in the basic magnesium carbonate-kaolinite system.

STRUCTURAL PHENOMENA IN CERAMIC-METAL NANOCOMPOSITE MATERIAL

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Silver addition effects on (Bi)-based high T_c ceramic powder was investigated from the viewpoint of structural and morphological phenomena in nanocomposite particles formed through aerosol reaction. The aerosols were generated from nitrates precursor solutions using ultrasonic atomizers operated at 1.7 and 2.1 MHz. Cation ratio in high Tc phase was fixed to be Bi:Pb:Sr:Ca:Cu = 1.8:0.2:2:2:3 and weight ratio of silver in composite was 20 %. Control over particle structural properties was established by adjusting some of the droplet/particle decomposition parameters (aerosol droplet density 8.28×10^7 droplets/cm^3, droplet velocity 0.02 m/s, max temperature 840°C, nitrogen atmosphere and variable residence time). Powders characterization was done using XRD, SEM and EDS analysis. Obtained particles have smooth surface, spherical shape, they are slightly agglomerated and the mean particle size is below 500 nm. The changes observed at the interfacial area at the metal-ceramic contact caused by the presence of uniformly distributed Ag nanoparticles affect ductile transformation, thermomagnetic stability and grain connectivity in (Bi)-based high T_c nanocomposites.

POWDERS FROM ZIRCONIUM DIOXIDE AND ALUMOMAGNESIAL SPINEL FOR THE PLASMA SPRAYING OF PROTECTIVE COATINGS

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The development of modern science and engineering demands much of constructional materials. They should run reliably for a long time in the conditions of drastic fluctuations of temperature, an effect of aggressive media, erosion and corrosion wear-cut.

Lately the protection of metal surfaces of some parts in machines and mechanisms with a help of stabilized zirconium dioxide, alumomagnesial spinel and high refractory materials based powders was widely used.

In the open joint-stock company "Ukrainian research institute of refractories named after A.S. Berezhnoy" the technology was developed as well as the manufacture of wide range powders of sieve fractions and micropowders on the basis of stabilized zirconium dioxide for a plasma spraying was mastered. The coatings from powders of a fraction 100–40, 90–40, 71–40, 63–40, 40–20, 40–0 μm on the basis of electrofused zirconium dioxide with a content (mass) — ZrO_2+HfO_2 not lesser than 90 %, CaO within the limits of 4–6 %, Fe_2O_3 not more than 0,3 % are characterized by high heatstability, wear — and corrosion resistance that ensures increased resources of the serviceability and it leads to the saving of high alloyed steels, ferrous and non ferrous metals.

An employment of protective coatings using the powders from stabilized ZrO_2 allows increasing considerably the operating temperature of engines.

As a result of carried out investigations at the open joint-stock company «Ukrainian research institute of refractories named after A.S. Berezhnoy» the technology was developed as well as the manufacture of electrofused powders for the plasma spraying on the basis of alumomagnesial composition and its solid solutions with corundum was mastered. The coatings from powders of fraction 100–40 μm on the basis of alumomagnesial spinel of two compositions with a chemical composition respectively Al_2O_3 — within the limits of 70–73 % and 74–78 %, MgO within the limits of 26–29 % and 20,5–25 %, Fe_2O_3 — not more than 0,3 %, Na_2O+K_2O — not more than 0,12 % and required fluidity are characterized by high electroinsulating properties: specific electrical resistance at 500 °C — $4{,}5 \cdot 10^7$ Ohm.cm. Protective electroinsulating coatings from alumomagnesial spinel based powders are most resistant in ionizing streams containing aggressive alkaline oxide and widely used in atomic power engineering.

PRODUCTS FROM ZIRCONIUM DIOXIDE STABILIZED BY YTTRIUM OXIDE FOR THE BRANCHES OF NEW ENGINEERING

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A rapid development of such new engineering branches as quantum generators using laser crystals of alumina – yttrium oxide group: precious artificial stones substituting for diamonds: fianite, garnets, and so on made necessary a manufacture of hightemperature heatinsulating ceramics with the service temperature up to 2300 °C.

In the open joint-stock company "Ukrainian research institute of refractories named after A.S. Berezhnoy" in seventies the study of a stabilization sintering and manufacture of the ceramics from ZrO_2 stabilized by yttrium oxide from 4 up to 15 mol % was carried out that allowed to work through the manufacture technology and to develop technical specifications which envisage the production of different types of products: rings, covers, crucibles, sectors. They are produced now by the institute. The products are manufactured as two brands TZIS-1 with Y_2O_3 content - 8–11 mass % and TZIS-2 with Y_2O_3 content — 22–25 mass % and open porosity up to 23 %. However these products possess insufficient thermal shock resistance. Therefore an improvement of this technology was undertaken and quality of these brands, at the expense of an introduction of monoclinic ZrO_2 addition were increased. We succeeded in manufacturing thermal shock resistant products containing both laid limited and increased concentration of Y_2O_3. At the expense of phase composition regulation depending on laid claims for products either with a high strength — 53–68 MPa or with high thermal stock resistance 8–11 heat cycles at 1300 °C — water or with intermediate values of such properties: with cold crushing strength 30–45 MPa and thermal shock resistance of 5–8 heat cycles from 1300 °C — water according to DIN 51066 Bl-1.

The prototypes of products from ZrO_2 stabilized by Y_2O_3 as blocks with a weight of 25–27 kg for the lining of a combustion chamber of in carbon black reactors with service temperature 2300 °C were produced and sent for testing. They are characterized by following properties: ZrO_2+HfO_2 content is 89,5 %, Y_2O_3 — 9,75 %, Fe_2O_3 — 0, 07 %, open porosity — 16–17 %, thermal stock resistance — 4–5 water heat cycles according to DIN 51068 Dl-1.

Institute manufactures nowadays the products of large assortment from zirconium oxide stabilized by yttrium oxide with a service temperature up to 2400 °C.

TOXICITY OF AEROSOLS OF ULTRAFINE HIGH MELTING COMPOUNDS (OF NANOPOWDERS) DEPENDING OF THE PARTICLE ELECTRONIC STRUCTURE AND MICROSTRUTURE

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The cermets production process may involve formation of elevated concentrations of ultrafine aerosols of high melting compounds within the operation zone, which shall pathologically affect the health of workers.

As the experiments on animals have shown, the toxicity of aerosols of ultrafine powders of high melting compounds is higher than that of coarse powders having similar chemical composition.

The aerosols of high melting compounds of d-transition metals with polymorphic structure of microscopic particles affect respiratory organs, produce albumen and nuclei metabolic disturbances, structure changes of interior organs. Ultrafine high melting compounds of non-metals with polymorphous microstructure produce a slight fibrogenic and generally toxic effect, whereas aerosols having fibrous-needle structure of particles cause a strong irritating influence on the respiratory organs and a strong desquamative bronchite can occur accompanied with formation of polypi in the bronchial tubes and pulmonary tissue, adenomatose structures, and potential cancerogenic effect.

Variation of the toxic properties of aerosols of nanopowders of high melting metals shall decrease with formation of d^5-configurations, and the decrease of non-localized electrons of atoms of metals, as well as the increase of sp^3-electronic configurations of atoms of non-metals.

Researches conducted by the Ministry of Public Health of Ukraine were used to establish maximum permissible concentrations for ultrafine aerosols of high melting compounds of transition metals with polymorphic microstructure of 2 to 4 mg/m^3 particles of 2 and 3 classes of danger.

The maximum permissible concentration for ultrafine aerosols of non-metals with fibrous-needle particle microstructure is
2 mg/m^3 marked by «K» (cancerogenic).

A MIXTURE FOR THE SYNTHESIS OF CUBIC BN

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Alkali metals and their compounds are extensively used as catalysts in the synthesis of boron nitride.

The investigation is concerned with the Li – B – N system. The aim of the work is the develop mixtures of lithium and boron – containing compounds that, after nitriding in an ammonium flow, make it possible to obtain complex compositions of the Me_xB_y – BN or $Me_xB_yN_z$ – BN type in wide range of concentrations for their further use in the synthesis of cubic boron nitride under conditions of high pressures and temperatures.

Amorphous boron and lithium carbonate, which is a cheap and nontoxic compound, were used as starting materials. The synthesis was carried out in an ammonium flow in the temperature range 800…1300°C. Products of nitriding were studied by chemical and X – ray analysis.

The effects of temperature, the exposure time, the rate of a gas flow, and the process of formation of complex compositions were investigated.

By varying the temperature conditions of synthesis and using mixtures containing boron and different amounts of lithium carbonate, we managed to obtain a number of products of nitriding consisting of hexagonal boron nitride and lithium borides of different composition (LiB_2, LiB_{10}), as well as BN in combination with lithium boronitride.

The action of high pressures and temperatures (≈5…8 Gpa, 1500…2000°C) on the synthesis products showed that, in the used mixtures, the degree of $\alpha \rightarrow \beta$ transformation was 40 mass%. In this case, in cubic boron nitride, the fine – grained structure is retained.

Thus, on the basis of performed investigations, the method for synthesizing the mixture for obtaining cubic BN in the process of formation of hexagonal boron nitride was proposed.

GRAPHITE – LIKE BN PREPARATION BY NITRIDING OF AMORPHOUS AND CRYSTALLINE BORON

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In this work we study an effect of various factors including crystal formation, dispersity and purity of boron powders, synthesis conditions and the activating additives on formation of boron nitride. The initial material are amorphous and crystalline boron powders; the activating additives are lithium carbonate and ammonium chloride. The synthesis is carried out at temperature from 1000 to 1400°C in nitrogen or ammonia flow.

The impurity content in boron powders is determine by spectrophotometer and photocolorimeter. The products of nitridation are examined by chemical and X-ray analysis, and electron microscopy.

Experiments show that degree of boron nitridation increases with increasing of powder dispersity and boron imperfection, as well as in the presence of boron oxide compounds and under reaction with ammonia.

The addition of lithium carbonate to all starting powders causes nitridation to speed up, and the degree of three – dimensional ordering of BN structure to increase. An optimal quantity of the additive is dependent on gas, that is N_2 or NH_3. 100%yield of boron nitride is attained even at temperature 1300°C/

Ammonium chloride is discovered to be a powerful additive for the synthesis from coarse-grained powders crystalline boron because of its amorphizing effect at high temperatures.

COMPOSITE ALN-SIC-Si_3N_4 CERAMIC POWDERS

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The development of composite ceramic powders of different composition enables to create materials with combination of useful properties for a wide application.

Hereby the composite powders with a covalent bond such as SiC, Si_3N_4 and AlN having the high strength, toughness coefficient and heat-conductivity are of great interest.

The SiC, Si_3N_4 and AlN composite powders obtained by carbothermal reduction of silicon oxide and aluminum oxide in nitrogen flow were the objects of investigation. Composite powders, containing SiC, Si_3N_4 and AlN phases as well as solid solutions of both AlN in α-SiC with its concentration up to 15 mass.%. and SiC in AlN with concentration up to 7 mass.% were obtained owing to the modification of technological regime. The grain size of powders depends on their composition. With the increasing of AlN content the size of powder particles increases from 0.1-0.2 μm to 1-3 μm.

Beside the equiaxial grains, the thread-like crystals of β-SiC with the diameter up to 1μm and the length up to 100 μm are formed . One can change the volume part of thread-like crystals from 0 to 30-40% by the process modification .

The powders of solid solutions above based on α-SiC and AlN as well as SiC-AlN and SiC-AlN-Si_3N_4 with different phase ratio were treated by hot pressing.

It was determined that the composite materials of AlN-SiC system had a high enough level of mechanical properties (σ_b-500-560 MPa, K_{1C}-8-9 $MPa \cdot m^{1/2}$) and a high corrosion resistance in the air up to 1500°C.

The materials developed have the fine dispersion structure with the homogeneous phase distribution. This structure defines the high level of their exploitation characteristics.

INTERACTION OF BORON CARBIDE WITH VANADIUM OXIDE .

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The composite materials of the B_4C-MeB_2 type exhibit high hardness, wear resistance, strength and chemical stability. These materials are prepared by sintering of mechanical mixtures of boron carbide with borides of metals or by boron - carbide reduction of oxides of metals where B4C is a reducer and remains one of the component of the composite material.

Previous investigations of the interaction of boron carbide with oxides of metals has shown that the B_4C-MeB_2 material can be prepared as a result of the solid-state reaction B_4C+MeC. This became the basis for the present work.

The interaction of boron carbide with vanadium carbide according to the reaction $B_4C+VC+B_4Si \rightarrow B_4C+VB_2+SiC$ was studied . The introduction of the B_4Si additive in the starting mixture was motivated by the necessity of binding free carbon which forms during the reaction . All experiments were carried out in the temperature range 800-1650 ^{o}C in vacuum. The interaction products were studied by X-ray phase analysis .

It was established , that formation of VB_2 occurs through the stages of formation of lower vanadium borides . As a result of the interaction between the disintegration products of B_4Si and carbon, SiC and secondary B_4C form.

On the basis of the experimental results , the optimum conditions for producing the material during reaction sintering were established. The composite material of the B_4C-VB_2-SiC composition with fine-grained structure was prepared.

Some physical properties of the material were studied.

CARBOTHERMAL SYNTHESIS OF ALUMINUM NITRIDE UNDER NITROGEN PRESSURE

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Aluminum nitride is extensively used for the production of functional ceramics. That is why the advancement of the technology of its synthesis with the aim of preparing high –purity powders with the controlled dispersity and morphology of particles is an urgent problem.

The effects of the dispersity and crystalline structure of Al_2O_3 and catalytic additives on the process of carbothermal synthesis and properties of AlN have been investigated in a series of works. Data on the influence of nitrogen pressure on reduction of aluminum oxide by carbon are not available.

In the present work an attempt to carry out the carbothermal synthesis of AlN under an elevated nitrogen pressure and static conditions was made.

Mixtures prepared from α-Al_2O_3 and carbon black were nitrided in the temperature range 1800-1900^{0}C under a nitrogen pressure of 0.1-0.3 MPa with an isothermal exposure for 2-3 h. Reaction products were evaluated on the basis of data of chemical, X-ray and electron microscopic analysis.

It was shown that the performance of the process under a nitrogen pressure $\leq$ 0.1 MPa did not practically lead to the formation of AlN, and the obtained powders contained 2 mass % N. An increase in the nitrogen pressure up to 0.2-0.3 MPa accelerated abruptly the reaction. The nitrogen content in the products of nitriding after an exposure for 3 h attained 32-34 mass %, which corresponds to 94-99 % AlN. Variation in temperature and in the carbon content of the mixture affected slightly the composition of the reaction products.

Samples with the smallest oxygen and carbon ($\leq$ 0.7 mass %) contents were obtained from a mixture with a stoichiometric composition at a temperature of 1800^{0}C and a nitrogen pressure of 0.3 MPa. The main distinctive feature of the obtained AlN powders is that they contain no fiber. The elevated nitrogen pressure suppresses the dissociation of Al_2O_3, eliminates the possibility of the reaction proceeding in the gaseous phase and favors the formation of AlN in the form of isometric particles.

PREPARATION OF BORIDES OF THE IRON TRIAD BY THE BORON-CARBIDE METHOD

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Borides of the iron triad are used in the composition of modern ceramic materials. Nickel borides, that are used as conducting materials in microelectronics and replace successfully silver, have found the most extensive application.

Interaction of metals with boron is a traditional method of synthesis of iron, cobalt and nickel borides, yet this method is insufficiently cost-effective because of using expensive starting materials.

Data on the preparation of these compounds by the boron-carbide method are practically absent in the literature. That is why, the aim of the present work is to investigate interactions of iron, cobalt, and nickel oxides with boron carbide.

The base of the work is a study of the reaction $MeO + B_4C + C \rightarrow MeB + CO$, where Me is Fe, Co, and Ni. Experiments were carried out in the temperature range 800-1700^{0}C in vacuum. The reaction products were evaluated on the basis of data of X-ray and chemical analysis. To simulate the chemical interaction in the studied systems, a thermodynamic calculation with using the ASTRA program was performed.

As a result of the investigations, it was established that the formation of boride phases begins at temperatures $\leq 800^0$C; in this case, oxides are completely reduced by boron carbide. In different stages of the process, borates of metals, boron oxide, carbon, metals, lower borides and carbides of Fe, Co, and Ni are present as intermediate products. Along with the main reaction, accompanying reactions proceed, for instance, the interaction between B_2O_3 and carbon with the precipitation of secondary B_4C; the evaporation of B_2O_3, with molecules B_2O_2, BO and B_2O_3 going in the gaseous phase. The higer borides are dominant in the reaction products at temperatures above 1300^{0}C.

It should be noted that, in the Fe-B, Co-B, and Ni-B systems, the number of boride phases increases in the following order Fe-Co-Ni (2, 3 and 4 phases, respectively), which is connected with the electronic structure of the metals. The more the number of boride phases in the system the closer they are in boron content. The results of the investigation are in agreement with this. It was shown that, with the method of boron-carbide reduction of oxides, practically monophase FeB as well as CoB and NiB containing impurities of lower borides in quantities of no more than 2-3 % can be obtained.

SYNTHESIS OF NANOOXIDES IN LAMINAR TWO- PHASE FLAMES

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In this work the combustion process for producing of the metal oxides nanopowders are considered. The synthesis method (which was named gas-dispersible synthesis - GDS) is based on combustion of dust clouds of microsized (d_p ~1-30 μm) metal particles in a laminar plume. It may be premixed plume of the metal particles in air (or mixture of an oxygen and inert gas) - like Bunzen's burner or non-premixed two-phase plume - like Burke-Shuman's diffusion burner. The method GDS allows to produce oxide nanopowders of Al, Mg, Fe, Zr, Ti and any other metals, for which it is possible to obtain a self-sustaining two-phase plume. Synthesized non-particles of metal oxides have the spherical morphology, narrow gradation, average size of particles are 40÷100 nm. Size distributions for oxide nanoparticles of all metals were measured, and correlated by lognormal size distribution functions. The chemical purity of products of synthesis is determined by purity of a precursor and as a rule above it. The process description of non-particles formation and scheme of the experimental installation for research of a two-phase plume and production of metal oxide non-powders are discussed.

It is shown that each particle of metal in a dust flame represents the micro-reactor, in which a nanoparticles formation take place. The dispersible structure of combustion products is determined by a combustion regime of metal particles. If temperature in the combustion zone of a particle exceeds the boiling point of metal (Mg, Al, Zn), the yield of metal oxide nanopowder can reach 100 %. For particles with the heavily boiling (Zr, Ti, Fe), the oxides are formed with a size of particles near equal the initial combustible usually. Is experimentally proved the possibility of gas-phase combustion (under the temperatures of gas and the condensed phase in combustion zone which is lower than the temperature of the metal boiling) with formation of oxide nanopowders of this metals (average size of particles – 20 ÷50 nm).

The effect of basic macroparameters of a plume (fuel and oxidizer concentration, metal particles dispersion) and also thermal structure of the combustion zone on disperse and phase characteristics of combustion products have been investigated by experimentally for aluminum. For the definition of temperatures of condensed and gas phases in combustion zone the spectral methods were employed, and for analysis of the combustion products the disperse and x-ray- methods were used. It is shown, that nanopowder of aluminia (average size of particles 0.04-0.07 microns, γ-crystal phase) which properties depends little on variation of parameters of synthesis.

To obtain pure oxide powders by GDS method it is necessary to use not less pure microdisperse metal powders which are frequently obtained from the appropriate oxides. However, unique properties of obtained nanopowders, and also the technological virtues of the method GDS (very low expenditure of energy, has one stage, ecological cleanness) do a line-up an oxide - metal-oxide quite acceptable for a commercial production. The method GDS allows also to obtain multicomponent oxides by the burning of mechanical mixtures of metals or its alloys.

PRODUCTION OF NANOCRYSTALLINE COMPOSITE POWDERS IN THE ALN-TIN AND ALN-ZrN SYSTEMS

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The modern methods of "chemical mixing", widely used in oxide systems enable to produce the nano-sized composite powders with the uniform distribution of phase components. In nitride systems similar technique is not developed.
The method of "chemical mixing" for obtaining the high-pure and homogeneous AlN-TiN and AlN-ZrN composite powders, using TiAl, $TiAl_3$ and $ZrAl_3$ intermetallics as phases-precursors in which initial elements are mixed as a regular structure, is proposed in the present paper; the nitriding of these intermetallics in both nitrogen and ammonia at 600-1400°C is being investigated. The reaction products were studied with the aid of chemical and X-ray analyses, as well as SEM and IR-spectroscopy.

It was shown that Ti and Al react with nitrogen practically simultaneously in the ratio determined by their concentration in the initial intermetallic. This fact is owing to approximately the same values of free energies of TiN and AlN formation. The nitriding of $ZrAl_3$ is accompanied by appreciable aggregation of nitride phases particles precluding from their fine and uniform distribution; in the same time the aggregation of the nitride phases formed at optimum regime of TiAl and $TiAl_3$ nitriding does not take place. The nitriding may be described by Avrami kinetic equation because it is implemented, mainly, under conditions when the reaction product does not exibit considerable diffusional resistance due to their specific structure: the isometric polyhedral crystals of TiN (20-100 nm) are distributed uniformly in the bulk of fine needle-shaped AlN crystals with a length of 100-500nm. The lattice parameters of nitrides are close to the reference data, IR-spectra testify that the interaction between nitrides phases does not occure.
The investigation fulfiled showed that it is necessary to carry out the nitriding process at the temperature as lower as possible (1200-1300°C) in order to fabricate the nano-dispersed AlN-TiN composite powders with an uniform distribution of components. It permits to preserve the elements distribution close to phase-precursor and to prevent to the growth and aggregation of phase components of composite powders. High purity, dispersity and homogeneity of the nano-sized AlN-TiN composite mixtures obtained by nitriding of TiAl and $TiAl_3$ intermetallics allow to prepare samples from them with high density (> 93%), strength and fracture toughness by sintering in nitrogen without imposing pressure.

PHASE INTERACTIONS AND PROPERTIES IN THE SYSTEMS $HfO_2(ZrO_2)$-Y_2O_3-Ln_2O_3

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The systems $HfO_2(ZrO_2)$-Y_2O_3-Ln_2O_3 (where Ln= La, Ce, Sm, Eu, Er) have been studied on melted and annealed samples in the wide range of temperatures (1250-3000 °C) and concentrations. These systems are perspective from the standpoint of creation thermal barrier coatings, fuel-cells, high refractory materials and ones with increased strength characteristics in which the composition of both matrix and strengthening phase is the same.

The samples for investigations in these systems were prepared by (1) hydrothermal high-temperature hydrolysis; (2) coprecipitation of hydroxides of aqueous and alcoholic solutions of Hf(Zr), Y and Ln nitrates; (3) evaporation and calcination of the mixtures at 1200 °C for 2 h.

The phase composition of the samples were investigated by electron-microprobe X-ray analysis, X-ray diffraction, petrography. The microstructure of melted and annealed at 1250, 1450, 1550, 1600 and 1900 °C samples was examined mainly by electron microscopy.

The crystallization of the alloys was investigated using the data on the structure of the liquidus and solidus surfaces. The crystallization paths for the alloys and the schematic of the reactions are constructed. The equilibrium phase diagrams have been deduced.

It was found that rare earth oxides doped hafnia (zirconia) formed tetragonal (T), monoclinic (B and M), cubic (C, X and F), hexagonal (H) solid solutions as well as intermediate phases crystallizing in perovskite-type structure with rhombic distortions $LaYO_3$(R) in the systems $HfO_2(ZrO_2)$-Y_2O_3-La_2O_3 and cubic pyrochlore-type compound $Ln_2Hf_2O_7$ ($Ln_2Zr_2O_7$) in the systems with La_2O_3, Sm_2O_3, Eu_2O_3 and hexagonal $Zr_3Y_4O_{12}$ (δ) in the whole row systems ZrO_2-Y_2O_3-Ln_2O_3.

THE PRE-DIAGRAMS METHOD FOR OPTION OF COMPONENTS OF A CERAMIC MATERIALS ON THE BASE OF DIOXIDES A d-METAL

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The Method was elaborated for a quick pre-diagrams options of the mutual solubility of components in a solid state by means of the local-energetic analysis of AMPEI-figure nets. Such abbreviation is common for some parameters, but PElCh=f(En,R) (En -electronegativity, R - atomic radius) is only discussed now.

If the PElCh-value for hypotetical pair-combinations "oxygen - metal" and "metal – oxygen" are [1]:

Systems	22 Ti	40 Zr	41 Nb	50 Sn	73 Ta
$O_2 \rightarrow$ met.	–296,503(–)	–20,058(–)	–157,873(–)	–7,527(–)	–132,6(–)
Met.$\rightarrow O_2$	+111,224(+)	+6,341(+)	+54,890(+)	+3,190(+)	+49,8(+)

then CEC (coefficient of energetical (isomorphical) compatibility of oxides) will be defined by dint of relations beetwin of them accordingly:

CEC	–2,6658(–)	–2,8796(–)	–3,1632(–)	–2,3596 (–)	–2,6637(–)

The problem of a profitable mixtures of them will be discused in report depending upon the PElCh – signes*.

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*AMPEI – auxiliary microscopical parameters of mutual-energetical influence; the first sign to a PElCh-value, – points out on an energetical contribution of admixture atom, but sign after of one - points out on character of a volume distortions, wchich forms second atom.

APPLICATION OF ENZYME IN PROCESSING OF ALUMINA POWDERS

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One of the most promising strategies to obtain less-defective samples from alumina powders, is the wet processing rout. Due to better control of powder-particle interaction and increased homogeneity of particle packing in the wet stage, lesser and smaller defects can be expected in the final microstructure, as compared with dry processing. Many attempts have been made in recent years to improve ceramic processing by transforming homogenous powder suspensions into solid green bodies. This can be achieved either by consolidating the dispersion medium or by flocculating or coagulating the ceramic particles in the liquid medium. The new colloidal processing method for shaping ceramic components we were used. The Direct Coagulation Casting (DCC) process offers the opportunity to obtain ceramic samples of high mechanical strength and high reliability at low cost.

The process relies on electrostatic stabilized ceramic suspensions and it is destabilization by time delayed reactions. Enzyme catalyzed reactions may be used either to create salt at a constant pH or to shift the pH of the ceramic slip to the isoelectric point of the powder. Different enzyme/substrate systems are outlined, suitable for different alumina powders. The reaction kinetics of the liquid-solid transition can be controlled by the enzyme concentration and temperature.

In this work method of molding of alumina using DCC process is presenting. Alumina (A16SG of Aluminum Company of America) of a 0.5 μm mean diameter grain size and specific surface of 8.60 $m^2 \cdot g^1$, measured by the BET method, was used for casting. The casting slip was prepared by adding a surfactant (citric acid and diammonium citrate) to deionized water. After mixing of these components, Al_2O_3 was gradually added and stirred. The Al_2O_3 concentration in the casting slip was change from 55 up to 85wt.%. The mixing of the casting slip was carried out for 4 hours in plastic mills with balls covered with a plastic. For the internal shift of the pH of the suspensions either urease catalyzed decomposition reactions of urea or lipase catalyzed decomposition of triacetin.

The application of internal catalyzed reactions leads to the obtaining of green and sintered of samples characterized by very uniform structure, high density and mechanical strength, low open porosity and high Weibull's modulus of alumina ceramics.

TERMOSTABILITY TO OXIDATION OF POWDERS VC, NbC, TaC.

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Refractory carbides of metals use in structure of composites as abrasiv, heat resisting materials at high temperatures and in agressive environments. In connection with it is expedient to investigate oxidation of powders carbides Vb- of metals at 298-1000° C, as they are investigated, basically, in a compact kind.

Process of oxidation of powders carbides Vb- metals on air investigated in an isothermal conditions in an interval of temperatures 500 - 1000°C (exposition time at each temperature from 15 up to 220 mines.) and in non isothermal conditions on derivatograf Q-1500 with speed of heating of samples 5 and 10 K/mine. with simultaneous realization of the differrential -thermal analysis.

For researches used carbides Vb- metals of the mark «p» (98 %). The sizes of the investigated powders have established sedimantation by the analysis.. Has appeared, that in all powders the particles by the size 5-10 microns prevail. Structure of products of oxidation determined radiographic analysis on the device DRON-3. Have established, that at last stages of oxidation are formed the highest oxides of Vb- metals. Stability of samples to oxidation on air judged behind degrees of their transformation

We have determined also thermal effects of the investigated processes from the areas of DTA-curves and have compared from designed under the Gesse`s law. Have established, that they exothermical and correlate. among themselves.

From a TG-curve have established, that at oxidation there is an increase of weight. The transformations, designed from these curve degree, carbides Vb-metals (speed of heating 10 K/mine.) given below.

VC		NbC		TaC	
T,°C	α (%)	T,°C	α (%)	T, °C	α (%)
481	1,12	369	0	500	0
519	1,40	469	15	610685	8,5
559	1,68	548	28,1	718	10
775	6,74	762	78,7	800	14,5
840	10,1	930	100	900	24
900	11, 8			1000	38
1000	15,17				

The high thermostability to oxidation carbides V and Ta on air is connected to formation dense superficial film their the highest oxides.

ROLE OF ULTRA- AND NANO-SIZED POWDERS IN FUNCTIONAL CERAMICS

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The transition of the particle size from micron to nano- fields, when the so-called sized effect is taken place, determines the specificity of solid fundamental properties. This effect can be positive or negative sense for change of material functional properties, which have been prepared from these powders.

The different methods of ultra- and nano-sized powder production such as PVD and CVD will be discussed in this report. Structure evolution, the processes of coagulation and coalescence will be analyzed from the point of view of the correlation between the nucleation rate and the nucleus growth rate in the dependence of the conditions for chemical reaction.

As the examples of chemical interaction the reduction of metals from oxides, thermal decomposition, mechanochemical syntheses, electrochemical deposition of composite systems based on iron group metals will be discussed in this report. The basis for ultra- and nano-sized powder production in all of these methods is the correlation between nucleation rate and the nucleus growth rate. The high or low temperatures, high rates of chemical interaction, the external conditions promote the formation of Non-equilibrium state of particles at their growth. The important characteristic of nano-sized powders, which have been produced in very non-equilibrium conditions is their interaction with medium components. This is the reason of assembly formation with the wide distribution of particles by size.

The process of mechanochemical syntheses for nano-sized powder production included the stages of mechanical deformation and relaxation process. The systems based on refractory titanium and molybdenum carbides, which have been prepared by mechanochemical syntheses in high energy mill will be discussed.

COMBUSTION SYNTHESIS OF Si_3N_4/TiN COMPOSITE POWDERS

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The use of powders having high hardness, corrosion and wear-resistance, appreciable electrical conductivity, etc. in modern ceramic engineering is growing at an accelerated pace [1]. Composite powders are of great interest among them as they combine properties of two and more compounds. Nitride composites occupy leading positions from the practical standpoint.

The present work is devoted to self-propagating high-temperature synthesis (SHS) of TiN/Si_3N_4 powder at combustion of Ti_5Si_3 in nitrogen.

The studies carried out have shown that the use of Ti_5Si_3 as an initial material has appreciable advantage in comparison with Ti-Si mixture [2]. The higher melting temperature of Ti_5Si_3 ($T_{melt.}$=2400 K) guarantees high degree of conversion due to free penetration of nitrogen into the burning sample by infiltration.

The experiments were carried out using cylindrical samples 30-40 mm in diameter, in the nitrogen medium at pressure 0,5-50 MPa. It was shown that nidridation temperature for pure Ti_5Si_3 at nitrogen pressures more than 1 MPa reaches up to 3000 K, resulting to Ti_5Si_3 melting and incompleteness of conversion. For decreasing the combustion temperature one of reaction products (TiN or Si_3N_4) or both at once were added to the initial powder. At the 50 wt.% of the diluent the combustion temperature, as a rule, was less than 2000 K, thus providing the normal regime of synthesis. As X-ray analyses have shown, biphase products consisting of TiN and Si_3N_4 were obtained. According to microstructural analysis data average particle size of the powders were no more than 5 microns.

As a result of the researches carried out optimum conditions for synthesis of fine ceramic TiN/Si_3N_4 powders containing phases at ratios from 10/90 up to 90/10 wt.% were determined.

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SYNTHESIS OF SILICON NITRIDE UNDER THE ACTIVATED COMBUSTION MODE

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Silicon nitride (Si_3N_4) is one of major compounds on the basis of which new ceramic materials are produced, distinguished by high hardness, refractoriness, stability to aggressive environments, small coefficient of thermal expansion, etc. The great interest in this compound leads to development of new methods for its synthesis. The method of self-propagating high-temperature synthesis (SHS) occupy a highly important place among them. A few variants of SH-synthesis of silicon nitride are developed, which allow to control physico-mechanical characteristics of the product by changing the composition of the mixture used.

The present work is devoted to combustion laws of silicon in nitrogen at the presence of combustion promoters such as polytetrafluoroethylene, melamine, urotropin, potassium nitrate, ammonium fluoride and others. Studies carried out have shown that silicon nitride can be synthesized at rather low pressures of nitrogen (0.3-0.5 MPa) when powdered polytetrafluoroethylene is used as a promoter. Under these conditions combustion temperature changes in the range from 1700 to 1750 K, and a part of silicon nitride forms as thin fibres 0.1-0.5μm in diameter and tens microns in length. Silicon tetrafluoride, which forms at the early stages of the combustion, promotes the formation of these fibres. When potassium nitrate is used as an additive, the silicon nitride particles represent mainly as perfect hexagonal crystals with the diameter 2-10 μm and 10-20 μm in length. These crystals mainly correspond to high-temperature β-form of silicon nitride. When inorganic halogenides are used as promoters, one can observe joint growth of two (α- and β-) forms of silicon nitride.

Thus, investigation carried out allows to state with assurance that by changing the promoter type it is possible to control phase composotion and the morphology of silicon nitride.

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SECTION B. MODERN PROCESSES FOR MANUFACTURING CERAMIC PRODUCTS: MODELING; COMPACTION; SINTERING; TREATMENT; JOINING; ECOLOGICAL SAFETY **59-107**

PROCESSING OF CERAMIC NANOPOWDERS INTO BULK PRODUCTS

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The main applications of nano-phase ceramics were up to now in the preparation of coatings, as a binder, and only to a lesser extent in the production of bulk products because the production of bulk ceramics from nanocrystalline powders are difficult to control. However, the nanocrystalline structured ceramics is sometimes required to keep the functionality of the final bulk product, i.e. in ion-conducting ceramics used as oxygen conducting membranes, electrochemical reactors, sensors, components of batteries, components of solid oxide fuel cells, etc. The widely used ion-conducting materials are zirconia, sodium-beta-alumina, and perovskite type compounds. Gadoline-doped ceria (CGO), strontium-doped $LaMnO_3$ (LSM) are very recently used for manufacturing the ceramics for environmental application, i.e. in cleaning combustion off-gases of particles, consisting of the soot and soluble organic fraction, generally named particulate matter (PM) emitted from diesel engines. An electrochemical reactor acting as a trap for the continuous removal of soot particles from diesel exhaust gas has been specially designed for this application. The following nanocrystalline materials have been employed for this purpose: a CGO powder for a multichannel monolith production and LSM as an electron conductive coating and catalyst. The open porosity of such monolith should be above 70%. To obtain a material with such high open porosity it was necessary to add a pore former to the composition of the paste. Two types of waxes with a different particle size distribution were used as a pore former. An extrusion technique was selected for shaping of monolithic components. Methylcellulose A4M was applied as a temporary binder. As a sintering additive the Co-acetate was added to the composition of paste. The samples were extruded in the form of multichannel type monoliths of diameter 84mm and length of 150 mm. The green monoliths were first dried in a climate chamber with the regulated temperature and relative humidity and then sintered at 920-950°C for 1 h. Sintered monoliths were characterised by the total shrinkage of approximately 20%, porosity 72-74% and pressure drop between 65-95 kPa. A thin, hundred nanometres thick layer of LSM was deposited on the surface of the monoliths by in-situ reaction of the starting chemical components. The silver electrodes were attached to the monoliths. The performed measurements showed an efficiency of above 90% for soot removal at low flow rate and 75% for high flow in the temperature range of 250-400°C.

RECEPTION, PROPERTY OF A GLASSCERAMIC IN MAGNETIC FIELDS

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Opportunities of application of magnetic fields (MF) in the "know-how" of a glassceramic are not studied well now. Possessed experience of applications can not receive a wide circulation owing to poor experimental and theoretical development of this question. With the purpose of finding - out the mechanism of influence MF on reception, the physicochemical processes of formation of structure of a glassceramic in operation examinations of physical properties (conductance s, microhardness, magnetizability (MP), IK, EPR, CMR CXP-200 "Брукер") materials on the basis of a glass, lanthanum, titanate, zirconat lead are carried out. Initial mass was plotted from chemical agents of the mark ЧДА and was synthesized in platinic tigljah. Then glassceramic was prepared, which glass transition was carried out in MF of various intensity (90, 180, 360 кА m^{-1}). At measuring MP on self-acting weights of Faraday the identity was observed is model in MF of weights of Faraday and in MF of an electromagnet at a stage of a glass transition. The received glassceramic in MF has allowed to reduce temperature of synthesis, to reduce of % the content zirconat lead and to gain more ecologically pure ceramics. From intensity MF is found, thus the activation energy does not depend on a mode TMA, that specifies relative changes of a degree of a disordering of a lattice and proves to be true by character of dependence of a microhardness from a mode TMA. Change MP have shown, that the quantity MF at formation of a glassceramic influences concentration of paramagnetic flaws. The effects of a X-ray diffraction analysis have shown decrease of the content of crystalline phases received in a glassceramic in MF. The microstructural examinations have shown, that glassphase settles down on boundaries, cementing grains and raising mechanical properties of a material, that proves to be true by the line, found by us, EPR. The analysis of spectrums CMR on samples has shown, that descends changes of a relation of components of an integrated spectrum environment, relevant to various phylum's, of atoms. The blanket reference feature of explored physical properties is the not monotonic view of dependence of their changes from intensity MF, the saturation is reached at 0,15 Tl. Further magnification MF the effect of action does not variate. The change of intensity and bias of a maximum of uptake is characteristic of spectrums of IK-uptake depending on intensity MF at formation of a glassceramic, that testifies to change of character of a micrononuniform constitution of a glassceramic from TMA. The received materials were used for manufacturing knots in a ultrasonic and optical gamut.

INVESTIGATION OF THE PROPERTIES OF NON-METAL NITRIDE POWDERS AFTER HYDROGEN-THERMAL PROCESSING

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Low concentration and low mobility of defects as well as low rate of diffusion processes are peculiar for crystal lattice of non-metal nitrides. Moreover, the considerable powder surface is passivated with atoms of chemisorped impurities which deteriorate the sintering. Therefore to obtain porousless materials the sintering processes must be activated. Both physical processes (which are directed to forming different defects and to their relaxation during sintering), and chemical reactions (related to the new phases formation during sintering) create the foundation for the activation methods.

A principle new approach to the sintering activation is proposed by the authors. This approach consists in hydrogen-thermal treatment (HTT) of precursor non-metal nitrides powders at 1000 °C over hydrogen and catalysts. The goal of HTT of powders is to extract the irrelevant impurities, to grind the powder particles and to improve the powder structure. The use of such powders allows to improve the technology of materials production and to develop new materials of assigned structure and necessary service characteristics.

HTT of Si_3N_4 and AlN powders was shown to favour the removal of sorbed impurities from the particle surface. This results in purification and loosening of powder particles aggregates. Moreover, HTT of powders leads to descent in starting temperature of powder sintering. The effect of HTT on the processes depends on the following factors: dispersity and phase composition of powder, and type of chemical binding in substance. The influence of the first factor is displayed in the case of Si_3N_4. This powder contains the metastable phase (α-modification). The sintering of such powder already at 900 °C is defined both by high powder dispersity and by developing the initial stage of $\alpha \rightarrow \beta$-phase transformation. Phase transformation always causes the activation of mass transfer processes. The sintering of Si_3N_4 begins at 900 °C and for AlN the sintering does not proceed even at 1150 °C. This can be explained by type of chemical binding (and therefore by value of interatomic binding energy): Si_3N_4 has more covalent bond type in comparison with AlN.

INVESTIGATION OF THE PROPERTIES OF SiAlONs DEPENDING ON THEIR COMPOSITION THROUGH THE USE OF SIMPLEX-METHOD

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The simplex-lattice plan of the fourth order involving 15 experiments was chosen for examination of composition influence on properties SiAlONs.

The subarea with pseudo-components in vertexes Z_1, Z_2 and Z_3 was investigated which one acted as silicon nitride (Si_3N_4), alumina (Al_2O_3) and aluminium nitride (AlN).

Design of an experiment using simplex-method makes possible mathematical models establishing a link between SiAlON composition and its properties, to optimize a composition of the material.

DENSE STRUCTURE FORMATION OF NITRIDE CERAMICS UNDER SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS

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The main two factors that determine density of nitride ceramics synthesised by self-propagating high-temperature synthesis in "gas-solid" reactive systems was found experimentally:

- volume change during nitriding, dominating in case of synthesis BN-based ceramics;

- sample shrinkage caused by pressure gradient of reaction gas (nitrogen) around combustion zone. The last factor is most valuable for densification of such ceramics as TiN, TaN, AlN, α- and β-SiAlONs.

The intensity of sample shrinkage simultaneously depends on nitrogen pressure in SHS reactor, starting sample diameter, content of combustible and low-melting component in green mixture. In some systems sample shrinkage is accompanied by plastic deformation of product. For example, the β-sialons grains decrease and obtain irregular shape with distorted boundaries, completely losing their traditional morphology of elongated hexahedral prisms. At same time the X-ray structure analysis data show disordering of their interlayer space along crystal c-axis.

In all considered reactive systems the most favourable conditions for synthesis of high-dense ceramics with uniform structure was realized under high-pressure nitrogen (100 MPa and more). Under such conditions the infiltration combustion fully transform to the layer-by-layer mode and the combustion parameters (burning velocity and combustion temperature) attain their maximum values (u_b=1,5–9 mm/s and T_c=2300–2800 C). As the result we was successful in obtaining nitride-based ceramics with relative density 0.9 and higher.

This work is supported by the Russian Foundation for Basic Research (project no. 99-03-32258).

THE USING OF THE NANOTECHNOLOGY IN DEVELOPMENT OF ALUMINA SPINEL/PERICLASE-BASED CERAMIC MATRIX COMPOSITES

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Recently, large interest has focused on nanostructured ceramic materials. Those ones are polidisperse fine particle systems which can be especially created by addition of particles with the sizes scale below 100 nm. The properties of these materials are superior to conventional ceramic systems having grain structures on a coarser size scale. In the papers [1] the technology of periodic wet ball-milling of alumina spinel contenting 6 wt % of periclase in $MgCl_2$-aqueous solution was described. The aim of such a wet ball-milling is to obtain a highly concentrated ceramic binder suspension (HCCBS) as a matrix for refractory castables. After wet-milling the content of nanoparticles in matrix composite was about 3%. After firing of such matrixs at temperature 500 °C the particle distribution was analysed once more: the amount of nanoparticles has increased in 2,5 times. In the present work, the reasons of appearing of the nanoparticles are explained.

Two principles of the development of nanoparticles [5] in the wet-milling matrix systems were presented: 1) *mechanic-chemical wet milling* of the material in the chloride solution on the condition that solution and solid phase cations were equal (MgO, $MgAl_2O_4$, the aqueous solution $MgCl_2 \rightarrow$ cations Mg^{2+}); 2) *thermal dehydration* of magnesium oxichlorides and brusite that formed at the slow chemical reaction between of the constantly dispersing periclase and (OH^{-1}, Cl^{-1})- ions.

At the wet-milling and the dehydration process the periclase nanoparticles having ability to activated sintering at the lower temperatures were formed, and this would give a real positive effect on the strength of *in Situ* refractory castables with such matrixs. The sintering of matrixs with nanoparticles are observed at temperature 970 °C. In the dry-milling systems the nanoprticles were not found and the sintering of matrixs was started at the temperature above 1100 °C.

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ZIRCONIA – BASED CERAMICS ON THE WAY TO THE PRODUCTION PROCESS.

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Zirconia-based ceramics possess good strength characteristics, wear resistance, hardness and corrosion resistance. All these benefits make possible its application in elements of different friction units and also as an optic connector of fiber-optical communications (FOC). Due to unique electric physical properties of zirconia-based ceramic materials they find wide use as solid electrolytes in oxygen concentration sensors.

At the present time a demand for zirconia articles, both solid electrolytes and wear-resistant ceramics arose in Russia. At the same time the serial production of these articles is lacking, which is explained by the general state of economy.

At the FSUE "Obninsk Research and Production Enterprise "Technologiya" the works on investigation and creation of zirconia-based materials were carried out and nowadays many attendant problems have been tackled.

The production process for manufacture of finely dispersed powders with particle size no more than 1-2 μm, conforming to all requirements of production of ceramics with stable properties level has been developed.

The testing of solid electrolytes as a part of oxidation sensors in variable environment have been carried out under industrial conditions. The emf values of sensors are given as dependencies on testing time, property, phase composition and structure of obtained ceramics.

The rig testing of input modules with ceramic radial bearings made of zirconia for centrifugal pumps have shown the absence of wear traces. The dimensions of friction surfaces have not changed.

Thus the methods of manufacturing ceramic zirconia-based articles of different purposes have been developed at the FSUE ORPE "Technologiya" and nowadays the organization of a bay on their production is held.

MICROWAVE SINTERING OF CERAMICS BASED ON SI_3N_4 NANOPOUDER

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The possibility of Si_3N_4-Y_2O_3-AL_2O_3 dense ceramics production by microwave sintering at near – atmospheric nitrogen pressure has been studied. A roentgenoamorphous Si_3N_4 powder with specific surface of 80 m^2/g and particle size of about 25 nm was mixed in benzine with Y_2O_3 and Al_2O_3 (9 and 1 mass %, respectively) obtained by salts decomposition. Test specimens were prepared by semidry pressing followed by hydrostatic densification in the latex molds. Blanks sintering was carried out in gyrotron technological complexes at radiation frequencies 30 and 83 GHz.

The effects of sintering temperature and exposure time on ceramics density, microstructure and phase composition have also been studied. It is shown in the paper that maximum ceramics density (90-91 % of theoretical) is achieved after sintering for 30 minutes at 1750°C. In this case Si_3N_4 decomposition becomes evident even at 1150°C. Sintering at 750°C for 30 min results in 14-15 % mass loss, with 12-13 % mass loss occurring during the first five minutes which is probably caused by the formation and evaporation mainly of SiO.

α-Si_3N_4 and β–Si_3N_4 were crystallized in ceramics on sintering. The amount of β-Si_3N_4 increased with the temperature and time of sintering. Besides, elongated crystals of β-Si_3N_4 were formed in the material microstructure.

It is revealed in this paper that in the process of furnace sintering nitrogen pressure of 20 atm is enough to obtain near – theoretical ceramics density.

REGULIARITIES OF FORMATION OF SUPERCONDUCTING JOINTS BETWEEN BLOCKS OF YTTRIUM-BASED MELT-TEXTURED CERAMICS

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The top-seed-grown melt-textured $YBa_2Cu_3O_{7-\delta}$ (Y123)-based material (MT-YBCO) is very promising for cryogenic applications such as flying wheels, electromotors, frictionless bearings, levitation transport, etc. The existing technologies for production of MT-YBCO don't allow yet large enough high-quality and complex-shaped parts to be produced that retard the HTS large-scale applications and further development of HTS devices. Kimura et al. [1] proposed to produce superconducting (SC) soldered joints between bulk MT-YBCO blocks using Yb123 SC powder. Walter et al. studied [2] the welding MT-YBCO at a pressure of 0.5-MPa using Yb123 and Er123 powders. Zheng et al. [3] have successfully tried Tm123+Y211(25 %)-based previously prepared spacer layer material. But in all cases only some local places of obtained joining showed the SC properties that were comparable with those of MT-YBCO, so the further complex study of the process is of great importance.

We succeeded in obtaining SC joining between MT-YBCO parts with critical current density of about 12 kA/cm^2 (at 77 K in the self-field) using Tm123 powder (with no additions of Y211and preceding preparation of a melt-textured material). The joining were produced in oxygen at about 1258 K. The seam with high superconductive and mechanical properties forms if the rate of cooling is about 100 K/h, i.e. much higher than that of melt texturing (0.5 K/h). Too high rates of cooling or heating (about 200-400 K/h) led to cracking and warping of MT-YBCO samples, which causes a dramatic decrease in superconductive properties.

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TiN-BASED NANOCRYSTALLINE CERAMICS

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Sintering behavior of nanocrystalline titanium nitride powders and TiN based composites have been studied under both linear and rate-controlled heating regimes in vacuum. The non-linear temperature-time path of RCS results in more uniform grain structure than linear heating schedule during sintering. The final grain size around 50 nm and residual porosity less than 2 % is the best evidence of RCS advantages over linear heating rate regime (600 - 1100 nm grain size and ~6 %, respectively). The near fully dense and fine-grained rate-controlled sintered specimens demonstrated the highest hardness ~ 26±1.3 GPa and fracture toughness 4,2±0.2 $MPa \cdot m^{1/2}$. The dependence of hardness against heating rate, grain size, porosity and regime of sintering is a result of the present investigation.

USE OF NANOCRYSTALINE PZT- POWDERS IN PRODUCTION OF PIEZOCERAMICS

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The application of nanocrystalline PZT -materials opens new opportunities for creation of high-quality film-shaped piezoelectric elements and high-strength volumetric piezoceramics with controlled over a wide range of the operation characteristics.

In this report the producing of piezoceramic elements from high - disperse nanocrystalline PZT with the size of particles 20-25 nm are investigated. The nanopowder was made by a co-precipitation method with use of a number of physical effects including microwaves - heating.

During researches methods of moulding (compacting and slip casting) of nanopowder are elaborated: water slips compositions for film casting are specified; organic binders for compacting of ceramics bar and compacting conditions are chosen.

In comparison with the powder received by conventional ceramic technology PZT-nanopowder at the stage of article moulding is more sensitive to the organic additions, which are used as binders, plasticizers, emulsifying agents *etc.*

At the temperature interval 900 -1200 °C peculiarities of sintering of nanopowder ceramics with various initial densities of green compacts and concentration of glass - forming additions were investigated. The received results enable to decrease a ceramics sintering temperature and to expand a temperature range of it's microstructure formation. It allows as result to operate by electrophysical properties. So, for example, transducer fine grain ceramics with the improved mechanical strength was purposefully received for the high-power piezoelectric. Besides the reduction of sintering temperature considerably decreases evaporation of lead oxide. As result the ecology of PZT- materials production is improving.

The work is fulfilled executed with the STCU financial support.

OXYGEN VACANCIES IN TETRAGONAL ZIRCONIA

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The sintering, diffusion creep and oxidation of zirconium at high temperature are determined by vacancies mobility, that makes the calculation of energy of migration of oxygen vacancy actual. Early our calculations are given for cluster and cell modeling the electronic structure of the oxygen vacancies in cubic zirconia. The present work deals with to the cell simulation of the oxygen vacancy and split-vacancies in tetragonal zirconia (zirconia(t)), using the tight-binding theory.

In the given work, the basis system of zirconia made of one 5S-orbital and five 4D - orbitals of zirconium and three 2P- orbitals of oxygen atom of zirconia. We use parameters consisting of values for diagonal terms e_s = -5.68 eV, e_d =-8.46 eV, e_p = -16.72 eV.

For calculations of energy levels of zirconia (t) in the absence of a defect, we have the used a cell of 12 atoms, inclusive the 8 oxygen atoms and 4 zirconium atoms. The center of cell was taken at the oxygen unit. For the oxygen vacancy, one simply removes the central atom of the cell. The nearest neighbour oxygen atom is displaced in the direction of a-axis or c-axis to central vacant unit, and then the calculations are repeated. Crystalline lattice parameters of zirconia (t) was taken a = 0.51053 nm, c = 0.51617 nm.

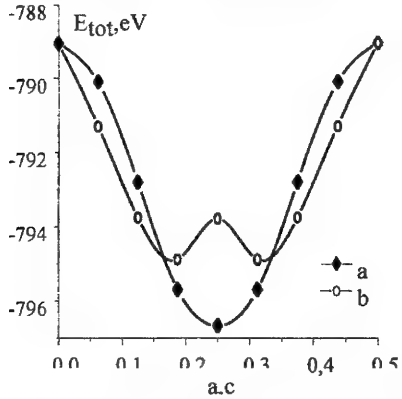

Figure 1. Total energy as a function of the displacement of the oxygen atom
a- *in direction of a-axis of zirconia(t),*
b- *in direction of c-axis of zirconia(t).*

A measure of the total energy of the system is given by the sum of the energies of all the occupied one-electron molecular orbitals. A rough estimate of the migration energy for the vacancy can be obtained by monitoring the total energy of the cell. For this we have calculated the total energy for the 12-atom cell with the oxygen vacancy as a function of the displacement of the oxygen atom in the directions of a-axis (fig. 1a) and of c-axis (fig. 1b) to central vacant unit.

We define a migration barrier of oxygen vacancy in direction of a-axis of zirconia (t), it is approximately Em_a= 0.92 Eg, and in direction of c-axis of zirconia(t), it is approximately Em_c= 0.71 Eg.

PROCESS MODELING OF OBTAINING CERAMIC PRODUCTS USING WASTE MATERIALS

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Production of construction materials takes one of the leading places among the material-intensive types. Thousands of tons of mineral materials, millions of cubic meters of gas and vast quantities of water are used annually at enterprises engaged in building material production. Therefore it is relevant to look for ways for reducing natural resources consumption through the use of waste materials.

A wide range of various types of waste coming from different kinds of production is known today as well as technologies for their utilization in ceramic production. The concentration of reusable substances and the amount of pollution agents released to environment may vary in these waste types. Besides, they are characterized by different scales of employment in the production process. The above mentioned factors may determine the amount of electric energy consumed, the product quality, economic aspects. Hence it is worthwhile to analyze the influence of such factors upon the technological production process as well as the ecological and economic characteristics. Therefore we suggest to use modeling through weighted graphs with corresponding weighting factors for the arcs. According to the goals set, the graph nodes may represent the following: reusable component proportion in the waste; amount of waste to be utilized; environment pollution; changes in the course of the production process; power consumption; product quality alteration; cost of the product made of waste. The values of weighting factors are given in points determined by specialists. Therewith a change of a characteristic by 10% implies a change of the weighting factor by 0,1 point. Apart from evaluation in points, the weighting factors may be represented in monetary units (price, environmental damage value, etc.). Basing upon the obtained values of weighting factors, plots are made allowing estimates of the changes in the production process due to qualitative and quantitative variations in waste.

TECHNOLOGY of RECEPTION of ELECTRODE MATERIALS FOR ELECTROSPARK ЛЕГИРОВАНИЯ

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The way and technology of reception of composite electrode materials for electrospark легирования (ЭИЛ) of a surface of steel details is developed with the purpose of reception противосварных (антиадгезионных) of coverings with reference to sites nuclear энергохимической of installation.

By development of an electrode material proceeded from the requirements, that the electrodes had sufficient durability at a stretching and bend, had good electroconductivity, is maximum допустимою electroerosion providing effective carry легирующего of an element on a processable surface and could ensure(supply) ЭИЛ at a vibrating or rotating electrode. Now similar material, which would respond all listed requirements, is not present. The creation of such materials is possible only by method of powder metallurgy. For reception of an electrode material by us was used карбид хрома $Cr_{23}C_6$. As metal связки have applied a powder хрома, which at sintering електродов in an air atmosphere and at Є of SILT forms connections with oxygen and nitrogen having high противосварными properties at contact to other metals. In шихту (електродную weight) the components as intermediate (burning out) organic binding and graphite were added also. Електродная шихта was moistened with a solution - binding up to пастообразного of a status, carefully mixed up and was pressed in cylindrical preparations by a diameter $1 \cdot 10^{-2}$ m and length $4 \cdot 10^{-2}$ m, which then were exposed сушке at temperature 393 - 473 K, низкотемпературному обжигу at 573 - 623 To and диффузионному to sintering at 1173 - 1223 K in current $1.8 \cdot 10^{2}$c with the subsequent cooling together with the furnace. Полученые electrodes had the high enough mechanical properties, well give in механичекской to processing by cutting or шлифовной (for example for improvement of contact with a jack электрододержателя or giving to the working end of the form of a cone).

The coverings, полученные at ЭИЛ with the help разработаного of an electrode material, have high durability of coupling with processable metal (product), температуроустойчивоть in working environment(Wednesday) реактора and have противосварными (антиадгезионными) properties.

EFFECT OF TiO_2 ADDITIVE AND POWDER CHARACTERISTICS ON SINTERING ABILITY OF ZIRCONIA NANOPOWDERS AND PROPERTIES OF CA-TZP MATERIALS

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A co-precipitation technique followed by hydrothermal crystallization was used to prepare zirconia nanopowders stabilised with CaO. The powders contained TiO_2 additives ranging from 0 to 1.5 mol. %. Two regimes of co-precipitation with NaOH were applied: i. at pH= 9.6-10.0, ii. at pH=12.3-12.7. The former one allowed the zirconia powders composed of nano-metric in size and isometric crystallites to be prepared. The latter one enabled to prepare nanopowders composed of a mixture of isometric and elongated crystallites. The morphology, phase composition and specific surface area of the powders were characterised using TEM, X-ray and BET method, respectively.

A method of dry isostatic pressing under 300 MPa were used to prepare green samples. Thay were pressureless sintered in an air or argon atmosphere for 2 hrs at temperatures ranging from 1200 – 1400 °C. The powders were also hot pressed for 1 hr at temperatures 1150 – 1300 °C under 25 MPa in an argon atmosphere. Densification and phase composition of the sintered bodies were characterised. Fracture toughness of the sintered bodies was determined using a Vickers indentation method. Electron microscopy was applied to characterise the microstructure of the sintered bodies.

The influence of TiO_2 additives and powder morphology on densification process, phase composition and mechanical properties of the materials was discussed. The comparison was made among the three methods of sintering of the Ca-TZP bodies with TiO_2 additive applied.

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MATHEMATICAL MODEL OF DEVELOPING THE MECHANICAL STRESSES IN GLASS-CERAMICS UNDER IRRADIATION

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One of the way of spent nuclear fuel immobilization is encapsuling it in protecting by the method of hot isostatic pressing [1]. The use of glass ceramics as a material for protecting forms is believed to be promising one.

For the RBMK spent nuclear fuel , encapsulated after 10 years of storing, the rate of accumulation a γ-irradiation dose by the glass-ceramic forms containing one RBMK fuel assembly is ~2.10^6 gray in year. Irradiation effect on the glass-ceramic material leads to increase of the glass phase density and to decrease of the crystal component density. This results in appearance of mechanical stresses and influence on the strength of a glass-ceramic form in total. Due to this fact the necessity arises to optimize the content of a glass and a crystalline phases in glass-ceramics.

The paper offers a mathematical model of behaviour under irradiation of a material in which the components undergo the volume changes being different both by the value and by the sign. The model considers a uniform distribution of spherical crystalline inclusions in the matrix from the glass phase. In a consequence of changing the volume of components under irradiation at the glass phase - crystal interface there appears the stresses: tensile ones in the glass phase and compression ones in the crystalline inclusion. The dependence of the glass ceramics stressed state on the glass phase volume fraction under different volume changes of components as a result of irradiation was studied. Within the framework of the model proposed it is shown that maximum tensile stresses in the glass phase increase linearly with increasing its volume fraction in glass-ceramics.

Analysis of stress dependency in glass-ceramics makes it possible to distinguish the range of a limiting glass-phase content from the viewpoint of resistance under irradiation: the lower limit (~25 vol.%) is determined by the requirement of the glass phase continuity in the model; the upper limit (~50 vol.%) is dictated by the sharp increase of stresses with a subsequent growth of the glass-phase content.

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PECULIARITIES OF THE PROCESS OF NANOCERAMICS PRODUCTION ON THE BASE OF DETONATION SYNTHESIS DIAMOND POWDERS

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A permanently raising level of requirements to the accuracy of production of components and units of machines, motors, turbines, audio- and video technique, etc. demands to develop a new class of tool ceramic materials productivity and a quality of treatment.

To produce tools meeting these requirements it is expedient to use ceramic specimen of a nanometric range, in particular, diamond powders of a detonation synthesis with a particle size 4-10 nm. However, when compacting an ultradispersive diamonds (UDD) in high pressure and temperature conditions there appear some difficulties connected with high particles dispersity, their big specific surface, a considerable quantity of adsorbed and hemosorbed impurities, the structure of the particles themselves.

The work investigated UDD compactivity in the field of catalytic diamond synthesis. It is determined that in conditions of comparatively low pressures and temperatures the properties of the produced compacts are determined mainly by the character of the recrystallizaion process of nondiamond carbon forms (graphite, carbon black) connected with the surface of UDD particles in dense carbon modifications. Investigation of the sintered specimen phase composition showed that in the process of UDD thermal treatment the following kinds of phase transformations take place:

- graphite - diamond allied carbon modifications - diamond;
- carbon black -diamond allied (amorphous) carbon;
- diamond- graphite.

The best physical-mechanical properties were obtained in specimens containing 3-5 mass. % of nondiamond carbon, therewith the compacts microhardness exceeded 60 GPa. The material structure evolution in the process of thermal treatment was studied as well.

In the experiments it was determined that in the process of UDD powders sintering, along with the regime of treatment, chemical and phase composition of the used powder, a configuration of a high pressure chamber and geometrical sizes of the source compact had a great significance. Calculations made for cylindrical blanks with different dimensions revealed a dependence of distribution of stress-strained state characteristics and, therefore, of the produce material properties on the compact geometry.

SINGULARITIES OF SHAPING OF A STRUCTURE COMPACTS FROM POWDERS BORIDES OF TRANSITIONAL METALS AT AN ACTIVATED SINTERING

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In work an influence crystallochemical singularities of a structure of borides powders on their densification at an activated excess of a boron a sintering in conditions of high-speed heat and short-term isothermal self-controls was researched.

By researches of a modification of compacts shrinkage at an induction sintering in a atmosphere of helium under pressure 10^5 Pa is established, that the components of a boron activate densification at a sintering already at temperatures $\geq$ 1650 °C. The detail analysis of a microstructure of sintering at temperatures 1650 - 2200 °C compacts TiB_2, ZrB_2 and HfB_2 with the components of a boron has shown, that they consist of three phases: pores, boride of transitional metal and rigid solution of transitional metal in a boron. The microstructure of sintering compacts at the components of a boron $\geq$ 5 mas.% differs by that already at T $\geq$ 1700 °C for HfB_2 and 1800 °C for ZrB_2 the grains of a diboride phase have prolated grane form, and the relation between sizes in longitudinal and transversal directions rise in accordance with magnification of a volumetric amount of a phase on a base of borons and temperatures of a sintering, that testifies to a course of recryctallisation process of diboride grains through a liquid phase on a base of borons. The presence of a great of a liquid phase at the components of a boron $\geq$ 10 mas.% activates process of anisotropic growth of grains of a diboride phase so, that between prolated grains the borons will be derivated large pores partially completed by phase on a base of boron. As such quantity of pores in compacts especially more, than the grains of a diboride phase are more prolated, it is considered, that the formed them is connected to a course of recryctallisation process and fast growth of grains MeB_2 in direction <0001> of a crystalline lattice, that energetically is more favourablis, than diminution of a surface energy of a system owing to reduction of a surface gas - crystal. That is pressure, that will be derivated owing to growth of anisotropic grains MeB_2 in compacts MeB_2 - B, considerably exceeds pressure of capilarity forces directed on densification of compacts, that reduces in loss of the form and diminution microshrinkage of a porous body.

At temperatures of a sintering $\geq$ 2200 °C, when in compact the frame from grains of a refractory phase will be derivated, and also at lower temperatures in places, where diboride grains grow together with each other, the prolated grains turn to grains incorrect, but isometric form. Thus, is shown, that the anisotropy of a surface energy of crystals of diborides of transitional metals can have of a essential influence on densification and forming of a compacts microstructure from diboride powders with the components of an excess of a boron.

LEGITIMACIES OF A GRAIN GROWTH AT A LIQUID-PHASE SINTERING OF BORIDES CERAMICS IN REQUIREMENTS OF LARGE TEMPERATURE GRADIENT AND CONTINUOUS HEATING

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With the purpose of clearing up of a nature anomalously high speeds of contraction of powdered materials on a base of refractory boride compounds in conditions of zone melting, in work on model compacts of the lanthanum hexaboride and amorphous boron (5 vol.%) mix the kinetics of the growth process of a refractory component grain at sintering at the presence of a solution phase in a field of temperature gradient is investigated.

For this purpose cylindrical compacts with a porosity 35-40 % by a diameter of 10 mm and length 144 mm are heated up to a melting temperature, and then the stock material is moved concerning a inductive coil with speed 1-6 mm/min. Before front of a melting in compact the large temperature gradient 1000 K/sm is erected and the site in which the compact represents a framework from particles of a lanthanum hexaboride pierced conferred porous channels is formed. The porous channels are completed by a melt on a base of a boron with a melting temperature 2059 + 50 °C. During such sintering the particles of a lanthanum hexaboride move continuously heating up in a solution phase, temperature gradient, in which remains to stationary values.

To eliminate movement of particles concerning a solution phase, to short-term sintering (2,5 - 5 min) were exposed compacts fixed concerning a inductive coil, obtained by impregnation of a porous framework from particles of a lanthanum hexaboride by a melt on a base of a boron.

By the quantitative metallographic analysis is shown, that the grain size of a refractory framework on the order is less in a sintering compacts in conditions of continuous drive in a temperature fields rather than at the same concentration and temperature-time parameters of a sintering process in case of fixed compacts.

It is shown, that the size of particles of a lanthanum hexaboride at sintering in conditions of a continuous heating is increased in accordance with rise of temperature and time of contact interaction with a melt on a base of a boron in a corollary of passing of processes of diffusion coaliscention, recrystallization in a field of temperature gradient through a melt on a base of a boron, formation and dissolving of a solid solute of a boron in a lanthanum hexaboride.

By computer model operation of process of a grain growth is shown, that on the order smaller grain size of lanthanum hexaboride driving in a temperature field of compact is explained by passing of process of dissolving of a solid solute.

THE MECHANISM of SHAPING of STRUCTURE AT A DIRECTIONAL CRYSTALLIZATION OF EUTHECTIC ALLOYS OF SYSTEMS LaB6-MeIYB2

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With the purpose of clearing up of the mechanism of growth and opportunities process control is explored influence of movement speed and intensities of agitation of a melt, crystallographic orientation of a matrix phase, diboride type on the structural - geometrical characteristics of phase component directly - crystallized alloys of systems LaB_6-$Me^{IV}B_2$.

By methods of a stereologic microscopy and by the texture-difractometry analysis is shown, that irrespective of a diboride type and orientation of a seeding agent the rod inclusions of diboride mainly grow in a direction <0001> that <001> matrix phases to a chip coincide a direction of movement of a band of a melt, along an axis. The rejection of an fiber axis from an crystall axis is increased at change of orientation of a matrix phase from <110> and <111> at minimum speeds of movement of a zone of a melt. In chips brought up at heightened speeds $\geq$ 3 mm/min there is a structural inhomogeneity as single-phase LaB_6 strips on inferior boundary of them rod diboride inclusions change the arrangement from a horizontal rather flat solidified front to vertical. In accordance with increase of growth speed the amount of such strips, which formation is bundled from change of temperature gradient and infringement of concentration requirements of conjugate propagation of boride phases of an eutectic alloy is increased.

In accordance with increase of growth speed a diameter of diboride inclusions is diminished, and their amount and reorientation degree of a fibers among themselves is incremented. The rise of intensity the disalignment of a melt gives in magnification of the sizes of diboride phase under other invariable conditions, which testifies to the important role of the diffuse mass transport along a crystallization front at growth of such eutectic alloys.

At speeds of movement of a zone of a melt < 4 mm/min the maximal amount of inclusions and their minimum size is formed in alloys with minimum concentrating and most major diffuse mobility of metal ($D_{Hf}<D_{Zr}<D_{Ti}$).

As in a direction of growth the new rods occur in intervals between two next, that terminate the growth, and have the tightened extremity, affirms, that on the geometrical characteristics of phase component directly - crystallyzed composites influences the concentration supercooling of a melt, which quantity is determined by concentrating of a d-transition metal in an eutectic alloy, and its diffuse mobility before a crystallization front.

PECULIARITIES OF FORMING AND SINTERING OF LARGE-SIXED SHOCK-RESISTANT PLATES BASED ON SILICON CARBIDE

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At present hot-pressing technology is a traditional method for production of large-sixed ceramic shock-resistant plates based on boron and silicon carbides. However, ceramic products manufactured using this technology are rather high-priced due to the use of expensive equipment (e.g., graphite press molds) and large energy consumption. This reduces their competitiveness in the world market and necessitates searching for alternative methods of production of large-sixed products of technical ceramics.

In this connection, upon investigation of peculiarities of shape and structure formation of silicon carbide materials depending on the fractional composition of initial mixtures, binder contents and sintering conditions, we have developed a resource-saving technology for production of large-sixed ceramic shock-resistants plates based on a slip casting method. Within the scope of this technology, we have

- found the optimum particle-size composition of polyfractional charge mixture of silicon carbide powders;
- determined the quantitative and qualitative compositions of the binder based on heat-treated paraffin;
- optimized temperature-and-time parameters of the basic technological process stages, such as binder distillation, casting, and impregnation of half-finished products with a carbon-containing material;
- worked conditions for reacting sintering of ceramic plates which allow manufacturing products with a density close to a theoretical one;
- manufactured and tested production equipment.

Through testing of the control samples and the samples cut out directly from finished products, we have shown that as to the basic physical and mechanical properties including those responsible for strength and shock-resistance of plates, the silicon carbide material sintered following the proposed technology is practically competitive with similar structural ceramics obtained by hot pressing.

This method was used in production of large-sixed ceramic plates of various thickness, ballistic tests of which have proved the efficiency of their use in multi-layer combined shock-resistant barriers.

APPLICATION OF A WEAK CURRENT DURING THE PREPARATION OF POROUS SiC CERAMICS VIA A SHS ROUTE

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Porous SiC ceramics have been prepared using processes involving an SHS step (self propagating high temperature synthesis). The starting reactive powder was a mixture of graphite and silicon with a C/Si molar ratio between 1 and 1.1. The experiments have been performed on pressed samples (relative density ≅ 50%) at about 1400°C in purified argon. Two different methods have been developed. The first method involves heating at 15°C.min^{-1} followed by a short (less than 1h) hold at the maximum temperature. After an SHS step, which occurs during the heating ramp, the completion of the reaction is obtained by diffusion. For the second method, the compact is heated at 15°C.min^{-1} to 1400°C, and then a weak electrical current is passed through the sample for less than 20s. The power dissipated in the sample during this stage is between 0.1 and 300W, depending on the starting powder morphology. This is sufficient to complete the SHS reaction.

Both methods strongly enhance the porosity of the compacts. A part of this porosity increase is due to the difference between the molar volume of the product and the reactants ($\Delta V = 28\%$). The rest of the porosity increase is related to the reaction mechanism and to the morphology of the Si and C grains. Experiments performed with different silicon average grain sizes and graphite morphologies have shown the existence of a strong correlation between the microstructure of the reactive compact and the grain and pore distributions in the final ceramic.

The porosities of the ceramics obtained with and without the electrical current are respectively in the range 70 – 82% and 65 – 75%, depending on the reactive powders morphology. When the SHS reaction is complete, the ceramics are more brittle and exhibit larger pores. The size of these pores is related to the silicon grain size.

PHYSICAL AND MECHANICAL PROPERTIES OF NANOCRYSTALLINE TiN-Al_2O_3 COMPOSITES PREPARED BY HIGH-PRESSURE SINTERING

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Nanocrystalline composites based on titanium nitride obtained by sintering of fine powders under high pressures differ in higher density and microhardness. This makes them advanced for the usage as highly hard high-melting point materials for various applications. In elaboration of our recent works for obtaining such nanocrystalline materials in this study the results of the investigation of structure, density and microhardness of Al_2O_3-20% TiN composites, sintered under the pressures up to 4 GPa and the temperatures up to 1600 °C are presented.

We used α-Al_2O_3 as initial powder with the particle size of d_s~30 nm and the surface area S=48,5 m^2/g, prepared by hydrolyze of sheet aluminum with the following decomposition of hydroxide and plasmochemical TiN powder (d_s~80 nm, S=14 m^2/g). For the investigation of the microstructure and the chemical composition of the samples SEM, TEM and X-ray analysis have been used. Vickers microhardness was measured at loads of 0.25, 0.5 and 1 N.

Composites with relative density of 99.5 % and microhardness of 24-29 GPa (Load 1 N) and also highly dense α-Al_2O_3 ceramics (H_v= 32.0±2.2 GPa (1 N) have been prepared. The evolution of their structure and physical and mechanical properties depending on sintering regimes have been investigated. It has been shown that maximal microhardness is reached under the condition of the minimal growth of grains and high degree of densification. The increase of the sintering temperature of composites is accompanied by homogenization of the structure and recrystallization. Herewith the lattice parameters of Al_2O_3 and TiN increase from 13.0033 Å to 13.0092 Å and from 4.2395 Å to 4.2408 Å accordingly. The results of the investigation of the structure and the properties of ceramics are discussed as compared to the results, available in literature, for the materials obtained by other methods.

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REGULARITIES OF INTERACTION IN SYSTEMS OF SILICON CARBIDE – CARBIDES D OF TRANSITION METALS OF IVB – VB GROUPS OF PERIODIC TABLE

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One of the promising refractory compounds for the purpose of creation on its basis high-temperature alloys is silicon carbide. The most successful is use of fibers of SiC reinforcing inorganic "ceramic" matrixes. As a result of high sintering temperature (T>2273) of such materials silicon carbide must be compatible with different components, including carbide d of transition metals of IVB – VB groups . Earlier there were studied state diagrams of system SiC-B_4C, SiC-$Me^{IY-Y}B_2$, $Me^{IY,Y}C$- $Me^{IY,Y}B_2$, which are built according to eutectic type. Melting of silicon carbide is congruous in character and of course research of mechanisms of its interaction with carbides d of transition metals is vital. Technological preparation of specimens and thermal treatment have been carried out in accordance with technique described in works of Unrod V.I., Ordanyan S.S. Conducted metallographic and X-ray phase analysis as well as measurement of some mechanical characteristics of metallic phases indicate a lack of chemical interactions between SiC-TiC, SiC-VC. It has been shown that studied state diagrams is conditionally quasi- binary and they are described according to eutectic type of interaction. It has been determined the temperatures of eutectic transformation as well as a structure of glass compositions. Microhardness of individual phases of silicon carbide , titanium, vanadium is practically in accordance with reference values. For eutectic colonies values of microhardness differ approximately from 24,0 Gpa (system of SiC-TiC) and 22,5 $\pm$ 1,1 Gpa (system of SiC-VC). Under increase of dispersibility of component phases the microhardness for eutectic alloys falls. Based on results which were obtained during the study of systems SiC-$Me^{IY,Y}B_2$ it is possible to suggest that eutectic type of interaction is typical in investigated systems SiC-$Me^{IY,Y}C$.

There have been determined character of changing of eutectic temperatures for systems SiC-$Me^{IY,Y}C$, where there is an increase of melting temperatures and shift of eutectic composition towards strengthening of carbides d of transition metals.

AN INFLUENCE OF SIZES AND THE SHAPE OF SILICON PARTICLES ON THE SYNTHESIS OF SILICON NITRIDE BINDER IN SILICON CARBIDE CERAMIC

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In the given work an influence of sizes and silicon particles on the synthesis of silicon nitride binder in the composion of silicon carbide products was studied.

For the research specially prepared three probes of crystalline silicon with different sizes and particles shape were used. The crystalline silicon contained 98 % of main phase, up to 1 % of iron admixture, up to 0,4 % of aluminium and up to 0,5 % calcium. The probe 1 is characterized by the sizes of particles of 4–12 μm having irregular shape and partially aggregated. The probe 2 was characterized by the particles sizes of 10–20 μm having rounded shape, partially aggregated. The probe 3 had the particles sizes of 4–10 μm as thin plates with out any traces of an agglomeration.

Using mentioned probes of silicon the mixtures were prepared: silicon (75 %) and silicon carbide (25 %). From mixtures using a semidry pressing at the pressure 30 MPa the samples were produced and fired in nitrogen medium during 4 hours both at temperatures 1350 and 1370 °C and at 1450 °C traditionally used when firing such products.

Samples based on probe 2 had lower indices of properties compared with samples based on probes 1 and 3.

Samples based on probe 3 fired both at 1350 and 1370 °C and at 1450 °C had strength within the limits of 240–350 MPa.

The same samples compared with samples 1 had lower content of residual silicon (4,8–2,9 as against 12,9–8,1 %), more high apparent density (2,10–2,19 as against 1,95–2,05 g/cm^3) and nitrogen content (18–25 as against 9–22 %) after firing at temperatures 1350–1370 °C.

Obtained results are indicatives of the possibility of a real increase of silicon nitride synthesis completeness at simultaneous decrease of the firing temperature using a specially prepared finely milled silicon powder.

VACUUM HOT PRESSING OF LARGE-SIZE HARD ALLOY ITEMS

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The process has been developed for vacuum hot pressing (VHP) of large-size (2 – 100 kg in mass) items of hard tungsten carbide-cobalt alloys in graphite moulds.

The technology makes use of commercial hard alloy blends. To provide for the needed structure the carbon content of the charge is adjusted via adding colloidal graphite. The use of crushed sintered products was successfully tried.

The VHP process comprises three stages, viz., degassing, solid phase pressing and pressing with liquid phase available. There is a substantial distinction between the process of thin- and thick-walled item pressing.

The production process cost was substantially reduced via repeated usage of moulds. Use is made of a two-layer die that consists of a graphite insert and "carbon-carbon" ring.

A trial shop was arranged having five hot pressing machines and a single-batch production of large-size hard alloy items was organized.

DENSIFICATION, MICROSTRUCTURE AND ELECTRICAL PROPERTIES RESISTIVE LAYERS OF GRADED COMPOSITE MATERIAL IN FORMULATION SI_3N_4-ZRC OR SI_3N_4-HFC

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Advanced structural ceramics based on nitrides and carbides are well known candidates for replacement of conventional metal parts in gasoline and diesel engines and gas turbines. They have been widely studied in order to improve their mechanical, electrical and thermal properties. Recently ceramic matrix composite (CMC) materials with controlled electrical conductivity have been replacing metal parts in special electrical and electronic devices which not only increases the performance of these components but also the range of applications for advanced ceramics.

We established the morphology, distribution and size of conducting particles for structural pattern a two phases composite in dependence of purity and dispersity of the initial powder and on temperature and environment of sintering processes. The goal of this work is a systematic investigation of the sintering behavior, the microstructure, the electrical and mechanical properties of Si_3N_4 - ZrC and Si_3N_4 - HfC composites. Because the development of microstructure is influenced by processing and by physico-chemical interaction of constituents during sintering and because the properties are strictly related to the grain size of the dispersoids and configuration of conducting area in gradient composites, ZrC (HfC) powder in tree different grain distribution for two style sintered body and two gas environment of hot pressing process were used.

Dense Si_3N_4 - ZrC and Si_3N_4 - HfC composites with the ZrC (HfC) phase in the range of 5 - 50 vol.% were produced by hot pressing technique in the reducing (CO). Two types of ceramic items in the form of the three dimensional component and the functionally graded material were evaluated. The influence of densification parameters, amount and grain size of ZrC (HfC) particles and geometry of the functional zone on the microstructure, electrical resistivity was investigated. It was proved that the resistivity of electroconductive ceramics is strongly affected by the amount and morphology of the filling phase. An evident influence of the grain size distribution of ZrC (HfC) powders and morphology of particles of the conductive phase on surface temperature heating elements was ascertained. Was showed possibility to 2 times energy saving if resistive layer of graded heating elements with coarse grains may be achieved.

PREPARAION AND PROPERTIES OF SINTERING SILICON CARBIDE MATERIALS WITH SIALON BINDER

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Influence of Sialon (SiAlON) content, SiC grain-size and technology factors of manufacture on structure, physical and mechanical properties of sintered SiC – materials was investigated. The samples have been prepared from green α-SiC powder of the grade M60 (Zaporozhye abrasive plant) and synthesized powder of β-Sialon (Z=2).

The Sialon content (10, 20, 30 mas. %) and size SiC particles were variable in initial mixtures. Control samples were prepared by the method of thermoplastic molding and sintering in the inductive electric furnace at the temperature 1700, 1750, 1800 °C in nitrogen gas medium (N2).

The optimum conditions of the preparation SiC - materials are defined. The microstructure of sintering samples and its influence on strength and thermo resistance was investigated. It was established, that in investigated region the thermo resistance of samples increases with growth of the average size of SiC particles, however simultaneously the strength - decreases. The strength and the thermo resistance of material is increased if content sialon binder rises at the same size of SiC particles.

The influence of a composition and conditions of thermal treatment on the stress state of sintered and hot pressured composite samples was investigated by optical-polarization method.

The recommendations for use of designed materials in different areas of technique are given.

SURFACE INFLUENCE OF CONCENTRATED SOLAR RADIATION OF OXIGENLESS CERAMICS IN AIR MEDIUM

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The surface heating of ceramic materials in oxidizing air medium can be used for the solution of the following two main problems: the determination of their high-temperature corrosion resistance and the obtaining of new chemical and structural formations possessing improved physicotechnical properties in comparison with the initial material. Solar furnaces are very useful instrument for the investigation of such influences on materials due to the heater sterility the possibility to obtain high temperatures (above 3000^0C) in the air medium, unilateral and inertialess nature of the heating being adjustable easily.

The purpose of this work has been to carry out the comparative investigation of the influence of radiant heating upon structural state and some properties of ceramics in the systems SiC-TiB_2, Si_3N_4-SiC and Si_3N_4-TiN. The solar furnaces of the IPMS NAS of Ukraine with the concentrators of 1,0; 1,5 and 2,0 m were used in the experiments. The technology of the samples manufacturing and some methodical features of the investigations will be described in the address.

As the investigations has shown all the materials of the system Si_3N_4-SiC possess high resistance to the oxidation under the conditions of radiant heating up to the irradiation level 650 w/cm^2 and maximum temperature at the heating zone $\leq 1500^0$C. At this zone thermal erosion has not been observed and the nature of the oxidation with the formation of the thin oxides film depends upon the ceramics composition. The rise of the irradiation up to 1000-1200 W/cm^2 causes the formation of a crater, the fusion of oxide layers, the intensive dissociation of silicon nitride.

In the process of momentary heating the materials of the system Si_3N_4-TiN within the temperature range 1200 – 1300^0C there is the oxidation of titanium nitride, which is accompanied by the formation of rutile and titanium oxinitride. The period of their lattice increases with the temperature increase. The formation of rutile causes the decrease of material hardness and the formation of oxinitride causes its increase. Under temperature above 1500^0C fluid phase appears on the samples surface which consists of silicon and titanium disilicide.

The material keeps satisfactory strength on the surface under the temperatures up to 1200^0C.

Corrosion resistance of the system SiC-TiB_2 ceramics is less than the same resistance of silicon carbide as it was supposed. It decreases when the content of titanium boride increases.

RESEARCH OF DENSIFICATION OF CERAMIC POWDERS UNDER ACTION OF HIGH QUASI-HYDROSTATIC PRESSURES

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The regularities of process of densification of ceramic ferroelectric, piezoelectric and superconducting materials at high pressure from 1 to 10 GPa are investigated unsufficiently. The present work is devoted to the study of the kinetics of densification of powder medium at pressures from 1 to 10 GPa for ceramic materials: PZT, superconducting materials based on ittrium and thallium, dielectric materials based on $BaTiO_3$, $CaTiO_3$ and composite materials. The samples were prepared without plastizer and placed in the container of high pressure camera of a type "toroid". The cold quasi-hydrostatic pressure was carried out at pressure 1÷10 GPa during 30 minutes. The root-mean-square mistake of measurement of relative density was 0,8÷1,4 %.

The moving of substance during pressing is defined by threshold mechanisms (bingamous plastic- viscous medium). We suppose that factor of viscosity of medium linearly depends on pressure. We suggest the modification of the Mak-Klelland equation for the description of process of densification in the following kind:

$$d\rho/dt=3P(1-\rho)/4(\eta_0+kP)[1/[1-(1-\rho)^{2/3}] - 2^{1/2}\sigma_s/P \ln[1/(1-\rho)]],$$

where ρ - relative density equal to the ratio of average density at the given moment of pressing to theoretical density of a material, P - external pressure, $\eta=(\eta_0+kP)$ - factor of viscosity, σ_s-critical stress i.e. value of a threshold for movement of strains, which is necessary for overcoming in order to appeared strain loop was removed from pore to volume of solid state. The result of numerical integration of the equation with selection of values of factors has shown that in an interval of pressure from 1 up to 10 GPa the coincidence of experimental and calculated curves with accuracy 1 % was observed.

Conclusions: **1**. Kinetics of condensation of powder medium at high pressure 1-10 Gpa was investigated. The condensation of a material during pressing occurs due to mechanisms of weight carrying finding out itself during moving powder particulates as whole and during strains movement. **2**. The mathematical model of rate of densification of ceramic powders is offered in view of linear dependence of factor of viscosity on pressure. This model well describes process of densification at high pressure of some dielectric, piezoelectric and superconducting ceramic powders.

FEATURES OF THE NANOCRYSTALLINE POWDERS PROCESSING AND FORMATION OF "SELF-REINFORCED" MATERIALS IN THE SYSTEM ZRO2-Y2O3-CEO2-AL2O3

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The forming of self-reinforced morphology of the materials in the system ZrO_2-Y_2O_3-CeO_2-Al_2O_3 depends on the starting powders properties, methods of their forming and the thermal treatment conditions. It was found, that the features of the nanocrystalline powders processing are of prime influence to this process .

The purpose of this research is to define the mineralizer influence (AlF_3) on the properties of powders and materials in the system ZrO_2-Y_2O_3-CeO_2-Al_2O_3.

The researches were carried out on the nanocrystalline powders ZrO_2 - 7 mol. % CeO_2 - 1 mol. % Y_2O_3, produced with hydrothermal synthesis. The AlF_3 powder has added to the powder with mechanical mixing. The samples have thermal treated in the temperatures range from 600 ^{0}C to 1000 ^{0}C. It was found , that both the decomposition of the ZrO_2 (CeO_2,Y_2O_3) metastable solid solution and the formation of $Ce_2Zr_3O_{10}$ occur in the presence of AlF_3 under the thermal treatment of nanocrystalline powder. Moreover , the morphology of the powder is varied: the plates with various cuts and chemical compositions are formed.

The nanocrystalline powders of composition ZrO_2-7 mol. % CeO_2-1 mol. % Y_2O_3 containing of 5, 10, 20 wt. % Al2O3 were used for the determination of technological properties. These powders also have treated with AlF3. It was found, that the slips from these powders possess large water absorbing after such treatment, therefore samples can be formed with uniaxial pressing with consequent cold isostatic pressing. The density of green bodies was 0,4 from theoretical. The sintering have carried out for various conditions in the temperatures range from 1150 ^{0}C to 1550 ^{0}C. It was determined , that the variation of sintering conditions results in the modification over a wide range of the matrix phase composition (from 100 % T-ZrO_2 up to 100 % M-ZrO_2) and reinforced phase (from α-Al_2O_3 up to Ce AlO_3).

Modifying of the material phase composition results in the variation of K_{1c} from 6 up to 20 MPa.m ^{0,5}, that is dictated by various mechanisms of toughening acting in these materials.

APPLICATION OF SINTERING / FORGING FOR PRODUCING OF LAYERED MATERIALS IN THE SYSTEM ZRO2-Y2O3-CEO2-AL2O3

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The sintering / forging is based on the sintering under pressure of previously sintered samples . The process is effective under producing of materials with the particles size close to 1 micron. The processing of ceramics in the conditions of plastic deformation allows to receive the materials of complicated composition with the ultra-fine microstructure.

The purpose of this research is to investigate the possibility of producing with sintering / forging of multilayer materials from nanocrystalline powders in the system ZrO_2-Y_2O_3-CeO_2-Al_2O_3.

Starting nanocrystalline powders of compositions 96,5 mol. % ZrO_2-3,5 mol. % Y_2O_3 (P1) and 90 mol. % ZrO_2-8 mol. % CeO_2-2 mol. % Y_2O_3 - 10 wt. % Al_2O_3 (P2) are obtained with hydrothermal synthesis with steps of sol-gel technology. The primary particles size was 10 nm. The particles are assembled in "soft " agglomerates of the spherical form (5-10 μm). Slip casting of aqueous slips was used for producing of moulds of three kinds: two monolithic - from powders P1, P2 and multilayer (22 alternated layers from powders P1 and P2). Relative density of moulds is 0,39 from theoretical. Moulds were previously sintered on an air at the temperature of 1150 ^{0}C, 1,5 h. Relative density after sintering is 0,6. Samples are fine-grained, average size of grains is less than 0,5 μm. The monolithic samples thickness is 2500 μm and the layered samples thickness is 1500 μm.

Hot punching have carried out at the temperature of 1450 ^{0}C in conditions of the constant compressing loading of 8 tonnes. The relative deformation of monolithic and layered samples without destruction is identical (80 %). The thickness are 500 and 300 μm accordingly. The microstructures of monolithic samples were differed: P1 - "regular" (size of grains and pores is 0,3 microns); P2- the grains size is 0,5 μm, the pores size is up to 3 μm. The α -Al_2O_3 plates (size up to 2-4 μm) are recorded. The fine-grained structure with the grains size of 0,3 μm was formed at the layered sample in each layers. The precise boundary between stratums is not marked. The homogeneous fine-grained structure of the material and the absence of the precise boundary between layers after sintering / forging will allow to realise the advantages of the mechanical properties improving of layered materials in comparison with monolithic.

BRAZING OF ZIRCINIA CERAMIC TO METAL USING STANDART Cu-Sn-Pb-Ti FILLER

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Joining of ceramic materials to metals is an important technical problem. One of the most widely used joining method is brazing. For brazing of ceramic special active alloys are used, because ordinary brazing fillers don't wet ceramic materials.

In this work the standart Cu-Sn-Pb-Ti powder fillers was used, early it was applied for brazing of Al_2O_3 and Si_3N_4 materials.

Brazing joints of ZrO_2-ceramic to forgeable cost iron were fabricated, its mechanical properties was studied. The one stage and the two stage brazing methods were tested. On the first method the filler was applied in gap between joined details as the powder and after that the brazing procedure was performed, on the second method the previous metallization of ceramic surface by it filler was carried.

There is established, that two stage brazing gets better results — the strength of brazing joints is higher and the scattering of strength values is less then for one stage.

Hot Compaction of the Ceramics and Cermets Fine Powders

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Modern polycrystalline materials have to be divided among two large classes as condensed ones, being formed during solidification and crystallization of the melts, and as consolidated ones, being formed by way of densification and sintering of respective fine powders. Ceramic and ceramic-metallic (cermet) materials are related to the second class, being distinguished by complex imperfect structure connected with random particle packing at an initial stage in the formation of a material proper. In the hierarchic structure of materials in question a mesostructure, being intermediate between the macroscopic and microscopic one as well as causing the imperfection factor of consolidated materials, exerts in the most degree on their macroscopic behavior when the latter are affected by mechanical actions at the stages of their processing and following operation. As it follows from this standpoint, confirmed by experience, it is necessary to use the hot static and dynamic compaction of ceramics and cermets powders for the formation of their fine-grained structure, providing a necessary complex of their mechanical properties and operating characteristics.

The regularities for hot compaction of the powders of ceramics and cermets under static and dynamic loading are considered in the paper. Dynamic and rheological features of the process above are analyzed with the use of a rheological model for an open mechanical system involving an irreversibly compressible viscoelastic strain hardenable body. Both a theoretical analysis and experimental data for impulse hot pressing of cemented carbides evidence that reduction in oscillogram height as well as increase in the time of compaction take place when a viscosity of the porous body matrix is decreased. It is found that a change of control parameters in a dynamic system in the event of hot pulse extrusion leads to the onset of auto-oscillations relating to origination of limiting cycles. This phenomenon to the full extent is borne out by the experimental oscillograms for hot pulse extrusion of high cobalt containing tungsten carbide based hardmetal. Experimental data for the densification kinetics of metal-like and non-metal refractory compounds during hot pressing under actions of static pressure in isothermal and non-isothermal conditions are discussed. It is found that the compaction of non-metallic covalent refractory compounds during static hot pressing takes place in a narrow range of temperature close to the melting point. In this case the compaction of pure refractory compounds is characterized by a high activation energy. But the mechanism of the porous body matrix flow may be changed in the temperature range above.

The Effect of Structure on Mechanical Properties of WC–8 % Co Hardmetal Fabricated by Various Methods

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The effect of stereological characteristics of structure in a WC–8 % Co hardmetal being fabricated by sintering in hydrogen (commercial method), sintering in vacuum as well as by hot pressing (HP) on its basic mechanical properties is studied (Table).

Table. The structure and properties of WC–8 % Co hardmetal

Fabricating method for hardmetall	Sintering in		HP in vacuo
	hyd-rogen	va-cuo	
Specific inter-granular surface S_{WC-WC}, $\mu m^2/\mu m^3$	1,65	1,56	1,2
Specific inter-phase surface S_{WC-Co}, $\mu m^2/\mu m^3$	1,46	1,55	1,6
Mean WC particle size $\bar{d}_{WC}$, μm	2,4	2,2	1,9
Mean Co layer thickness $\bar{L}_{Co}$, μm	0,75	0,71	0,55
Contiguity C_{WC-WC}	0,43	0,31	0,25
Contacts number on a grain WC, N_c	3,5	2,6	1,9
Density $\gamma \cdot 10^{-3}$, kg/m^3	14,6	14,7	14,8
Vickers hardness HV_{50}, GPa	13,6	14,1	15,6
Electrical resistivity $\rho \cdot 10^{-8}$, $\Omega \cdot m$	20,7	18,9	17,9
Transverse rupture strength σ_{ts}, GPa	1,8	2,2	2,4
Compression strength σ_{com}, GPa	4,2	4,15	4,12
Impact strength a_k, kJ/m^2	40	50	62
Fracture toughness K_{Ic}, $MPa \cdot m^{1/2}$	8,0	11,0	12,1

It is ascertained that improvement of structural characteristics of the hardmetal in study leads to elevation of its mechanical properties. It is possible to explain increase of such properties as σ_{ts}, a_k, and K_{Ic} by reduction of S_{WC-WC}, C_{WC-WC}, N_c and increase of S_{WC-Co}. The same structural characteristics lead to reduction of resistivity ρ. It is possible to explain increase in HV_{50} of the hardmetal by decreasing the WC grain size. The applied external pressure during HP provides increase the hardmetal density.

PROBLEM OF AN ENVIRONMENT PROTECTION BY MANUFACTURE IN CERAMICS PRODUCT

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In manufacturing processes of ceramic materials, mainly of advance ceramics, auxiliary components (binders, solvents, plasticizers and others), which in subsequent should be completely or partially removed from ceramics are used. The latter as a rule are toxic and flammable.

The first step on a way of reduction of an environment contamination is transition from the organic solvent to water-based solvent. At that time the difficulties arisen caused by hydrophobility of the binders applied as well as the necessity of special treatment of the binders. An addition, the high temperature is needed for water removal than for petrol and other easily volatile solvent, and it leads to increase in energy expenditure .

The best variant of processing is that which use no binder, solvent and other accompanying additives at all. The constraining factor on this way is a bad ceramic powders formability (being prepared mainly by long milling). The paper concerning the study of powders formability of and nature of a strength for green preforms relate mainly to metal powders [1]. Thin tapes of pure cubic BN and various grades of graphite were fabricated by the author in 1985. Now it is possible to fabricate flexible strong green tapes of ceramic powders without binder [2], as well as the tapes of graphite powders (expliated graphite), which is applied to seal units [3].

The study of a strength nature for green bodies of ceramic and others non metallic powders fabricated without binders will enable to refuse from binders application and to reduce negative contamination effect on the environment.

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2 Menon M., Chen I-W. Bimaterial Composites via Colloidal Rolling Techniques: 1, Microstructure Evolution during Rolling // J. Am. Ceram. Soc. 82. N12. 1999. P. 3413- 21.

3 Пат. 2076085 Россия, МПК6 С 04 В 35/536, F 16 J 15/16. Волков В.Ж., Чевордаев В.М., Хохлов А.А., Хмелевой А.Н. Способ изготовления уплотнений. Опубл. 27.3.97. Бюл. №9.

FABRICANION AND APPLICATION OF THE LAYERED COMPOSITE CERAMIC MATERIALS (REVIEW)

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Various methods for fabrication of the separate layers of ceramic materials as a slip casting, casting on a driven tape, injection moulding, extrusion, rolling and other methods are considered. The advantages, lacks and limitations of applicability for each methods are marked. In particular, such advantages of the rolling method as an opportunity of fabrication of tapes with increased density and lowered contamination by additions of a ready product are marked. The question of the use water-based binders on a is considered.

The subsequent fabrcation of layered material consists either in manual stacking of various layers or in deposition of layer of early obtained one by one of the methods above. The further processing consists either in sintering, or in hot pressing multi layered ceramic material.

The results of researches on rolling of ceramic powders are given. The large is given attention to fabrcation of layers Si_3N_4 and TiN. The optimization of rolling (increase the strength and flexibility of green tapes and fabrcation of layers with by thickness from 200 up to 500 microns) enables to fabricate layered composites with internal stresses and as a result of it to raise their fracture toughness. The bifurcation of cracks in a layered composite during fracture is considered in detail.

The properties of materials being fabricated by various methods are listed. Among the letter the composites for cutting tools and structural parts, especial by in thermic stressed state. Other areas of application of such materials are considered. The prospects of their use are discussed.

A possibility for application of the straight line rolling of ceramic powders with the aim of creation of solid oxide fuel cells is now considered. For this purpose the fabrication of layers with the thickness of 50-100 microns is necessary.

Ceramic Materials to Work in Conditions of Erosion Wear

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An improvement of operational and economic characteristics determine a complicated complex of demands to products made from ceramics.

The present work is dedicated to a development of approaches to solve tasks on production of ceramic materials taking into account a variety of factors which accompany a formation of a structure and properties both in the process of material production and during exploitation of particles thereof. A tool used in units of crystal distribution during integral scheme production is presented as a product. Technological solutions of making a ceramic microtool are considered as an independent functional control subsystem with its own inner organization of objects and interconnections.

The microtool material is considered as a functional substance. There are determined the substance functions on each stage, beginning from the preparation stage of the source powder to the analysis of the product operation in the process of exploitation. Processes of dispersion and activation of the source change including aluminium oxide, magnesium oxide, aluminium silicate component, silicon nitride are considered in detail. The activation is considered as a «compulsory» increase of energy on structural components of the listed charge components.

There are considered technological ways of making products from ultradispersive ceramic powders.

It is shown that for the considered ceramic products operating in conditions of erosion wear it is necessary to have a definite combination of values of hardness and failure viscosity. Increase of hardness minimizes a degree of wear in the field of formation of a fatigue crack. Therewith a level of stress corresponding to formation of a fatigue crack lowers with an increase of hardness.

In the work there are presented results of investigation of wear-resistant and corrosion-resistant ceramics, containing euthetic additions of modifying oxides.

A practical meaning of the work is in a theoretical engineering and realization in practice of a ceramic product with the needed strength and wear resistant characteristics as well as corrosion resistance.

FORCE CONDITIONS AND ENERGY CONSUMPTION IN HOT STAMPING POWDERY BLANKS

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Knowledge of changing in deformation force and work consumption while stamping, being the most important characteristics, is required for optional choose of the fording and pressworking equipment. For this reason getting the analytic relationship to determine forces while deformation is the actual problem in calculating the technology for manufacturing powdery materials at decreased energy consumption.

Relationship of force in hot stamping powdery blanks which describes the process with a high accuracy has been obtained on the basis of the experiment and has the expression of

$$P = \frac{\pi R_0^2 \left(\frac{\Gamma i}{\chi \sqrt{3}} \right)^{1/n}}{\left(1 - \varepsilon_Z\right) \theta^{1.47}}$$

R_0 - initial blank radius; I'i - rate of deformation shearing; θ- relative blank density; χ, n - experimental coefficients; ε_Z - axial deformation.

The comparison of experimental data of force conditions during stamping with calculated values of force proves their convergence.

Maximum error on final stages of stamping is 7,5%.

Work consumption for deformation has been determined from load oscillogram obtained.

It was found that pressure and force grow and deformation work decreases when stamping less compact blanks. This is explained by the fact that with a growth of blank density their acceptable rate of deformation increases at first stage of the process and respectively the working stroke of a press slide.

Proposed relationship enables to make computations evident and determine deformation force of hot stamping with high accuracy that gives the opportunity to optimize the computations of the technology for manufacturing different powder materials and choose forging and pressworking equipment.

CONCENTRATED SOLAR ENERGY IS ECOLOGICALLY PURE SOURCE FOR MANUFACTORING GLAZED CERAMICS

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Thermal treatment of building materials stipulating for surface glazing and fusing requires considerable energy consumption. Natural gas and electric power not so often are used for these purposes usually. In the both cases directly in the process of treatment when gas is being consumed or indirectly when electric power is being produced there are such ecologically ill effects as atmospheric contamination by fuel combustion products, the increasing of greenhouse effect and others.

In the IPMS NAS of Ukraine for a long time the investigations of the possibility to use concentrated solar radiation (CSR) are carried out for realizing energy-consuming technological processes including the glazing ceramic facing files [1] the surface fusing of slag concrete and other building materials [2]. The CSR use in high-temperature processes enables not only to save energy but to eliminate completely ecologically undesirable influences upon the environment accompanying the consumption of traditional fuels. In this work the conclusion is made by means of an example of the processes adduced above also the surface fusing of light materials obtained out of frothed metallurgical slag, compact ceramics and analogous raw material of monolithic and grinded natural basalt, the glazing of art ceramics with applying a drawing by the transfer method, other processes and materials as to the prospects of the use of solar furnaces in this field under certain natural environment social and economic conditions. The data are adduced concerning energy consumption when the typical materials surface is being fused and the comparison of them with analogous indices in industry. The main specifications and the conditions for the creation of an industrial type solar furnace are formulated.

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THERMAL STABILITY OF ZIRCONIA CERAMICS FROM NANOPOWDERS

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Thermal stability of zirconia ceramics from ZrO_2+3 mol.% Y_2O_3 nanopowders obtained by the chemical coprecipitation with using of ultrasound, microwave and impulse magnetic field treatment was being investigating. The powder compaction was being fulfilled by hydrostatic pressing (100-1000 MPa). Structure and phase content was being studied by methods of X-ray analysis and electron microscope Mechanical properties are being determined.

It was shown that the sintering at temperature 1500^{0}C and 1 h heating is the optimal regime. In this case ceramics has small grained (grain size 0.2-0.3μm) homogenous structure with 100% tetragonal phase and 5.96-6.0 m^3/g density.

It was established that after 20 h annealing at 200^{0}C near 3% M-phase are appearing on surface of investigated of specimens. Further increase of heating duration to 2500 h does not lead to the phase content change both on surface and in volume of a specimen and degradation (softening) as well. It was proposed that stability of the investigated ceramics is ensuring by the small grain size, which because of increased surface energy hinders to the T→M transformation. In material of the same compound sintered at 1500^{0}C, which has grain size about 2 times larger, the content of monoclinic phase already after 20 h anneal at 200^{0}C is equals ~ 60% [1] (Fig.) and the sharp ceramics softening goes on.

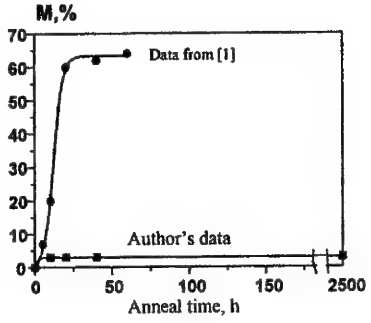

Fig.

It is established that using of coprecipitation technology with the application of high active physical actions and nanopowders compactions in conditions of high hydrostatic pressure allow to obtain the thermostable ceramics with the density ρ = 5,9 – 6,0 g/cm^3, bending strength σ_b = 900-1000MPa, coefficient of toughness at fracture K_{Ic} = 9 – 11,5 МПа·м$^{1/2}$ and Veibull modulus m = 10-18.

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TECNOLOGY 0F ZIRCONIA BASED NANOCRYSTALLINE POWDERS OBTAINING

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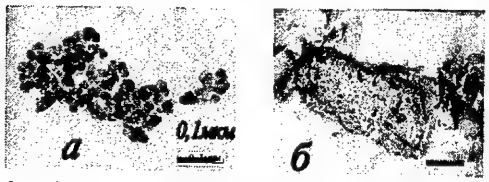
For ceramics production from zirconia based ceramic powders methods of chemical coprecipitation is most suitable. These methods allow to improve basic characteristics of powders, but even these methods do not permit without special methods to obtain properties of nanopowders dictating by the modern level of technique development.

We develop the methods of obtaining of powders with given properties with using of ultrasonic, microwave and impulse magnetic field treatment in chemical processes of synthesis. The effectiveness of these treatments application both one at a time and in complex is shown. The technology ensures:

- fixed chemical and phase content,
- homogeneity of components distribution,
- fine particle size (10-30 nm) and its aggregates (0.2-2μm)with possibility of the particlesand aggregate size controlling,
- agglomerate softness,
- high level of the ceramics properties and its stability;
- possibility of small additions inserting for properties improving and obtaining of ceramics of necessary colors;
- possibility of using for film technologies.

Basic characteristics of obtained powders: particles size - 10-12 nm, aggregate size 0.2-2 μm, special surface S_{BET} = 100-180 m^2/g, soft (<10 MPa) agglomerates, 100% of tetragonal phase. The structures of powders obtained by (a) developed and (b) standart technology< in which the coprecipitaion method was used, are shown on Fig.



The technology was realized in conditions of experimental-industrial facility, which gives possibility to obtain about 400 kg of powders per month.

Developed technology can be used for obtaining of the oxide nanopowder of other complicate oxide systems. Its tested for obtaining of powders of the $Pb(Ti,Zr)O_3$ and $La_{0,5}Ca_{0,5}MnO_3$ systems.

The work is fulfilled with financial assist of STCU.

SINTERING OF CERAMICS FROM ZRO_2-3 mol.%Y_2O_3 NANOPOWDERS

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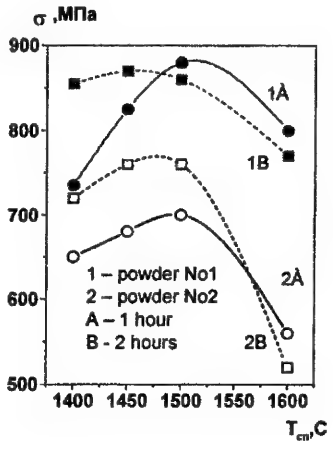
The work is devoted to sintering of nanopowders as peculiarities of structure and surface state of nanocrystals that can affect kinetic of ceramics sintering and properties.

Processes of sintering of two nanocrystalline ZrO_2+3мол.% Y_2O_3 powders with particles size 10 (powder No1) and 20 (No2) was being considerd. The compaction has been accomplishing by hydrostatic pressing. Peculiarities of the density change during sintering as well as dependence of structure and properties of ceramics on sintering temperature and compaction pressure were being investigated.



It was shown that at sintering of investigated powders, which consist of aggregated nanosized particles, the ceramics high density (95-98% of theoretical) is creating in account of intensive healing of nanosize intraaggrgate pores occupied about 40% of volume in sintering compact pressed by high hydrostatic pressure (500-1000 MPa). It was established that one-phased tetragonal ceramics with 0.3-0.5μm unixial grain is coming as result of the sintering at short heating (1h) at temperatures 1500^0C. The largest bending strength σ_b reaching in specimens from powder No1 to value ≥ 900 MPa (Fig.) and coefficient of toughness at fracture K_{1c} = 8.5 Mpa·$m^{1/2}$ correspond to such structure. The sintering at temperatures above1500^0C creates three-phased ceramics (tetragonal + 5-7% cubic + 4-5% monoclinic) with morphologically dual structure: cubic grains with size 2-4 μm on background of 0.2-0.5 μm tetragonal and monoclinic ones. Herewith the ceramics strength decreases to 750-800 MPa, while K_{1c} increases up to 8.5 MPa·$m^{1/2}$.

The conlusiont is done that it is possible to control properties of ceramics sintering from nanopowders by changing of the particle size of initial powder, compaction pressure and parameters of sintering regime.

INFLUENCE OF THE COMPACTION METHODS AND SINTERING CONDITIONS ON THE Bi,Pb-2223 SUPERCONDUCTOR PARAMETERS

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The density, porosity and critical parameters of the Bi,Pb–2223 high temperature superconductors were studied in the dependence on methods and conditions of their compaction and calcination.

The density of Bi,Pb-2223 superconducting samples (hydrostatic pressing, P~200-600 MPa) didn't essentially change and was equal 60-75 % from theoretical after sintering at temperatures of solid state synthesis (840-850^{O}C). The critical current density (j_c, 77 K, 0T) was 200-350 A/cm^2.

The increasing of sample density and decreasing of the linear sizes by 8-10% were obtained after annealing at 870-885^{O}C in presence of liquid phase arising from incongruent melting. The critical current density at 77 K was in the range of 0 up to 600 A/cm^2. The j_c values didn't markedly change after additional firing in air at the condition of 2223 phase stability (~100 h.) Introduction of easy melt oxides Bi_2O_3, Bi_2CuO_4, $Bi_{0,1}Pb_{0,9}O_z$, $Cu_{0,2}Pb_{0,8}O_z$, calcium halogenide or copper halogenide in quantities of 2-10 mass.% in most cases resulted in degradation of a phase 2223 and decrease of j_c.

It is established, that the pulse laser treatment (microsecond impulse of 1-3 J/cm^2 capacity) didn't essentially influence the critical parameters Bi-ceramics with thickness of 1-5 mm. The increasing of capacity (4-6 J/cm^2) and duration of irradiation stimulated the decreasing of the critical parameters. Melting of a surface Bi,Pb-2223 ceramics by laser irradiation helped increasing of microhardness of the samples 3-4 times.

The increasing of the sample density was achieved after hot compacting in graphite mould at pressure 300 MPa, but the j_c values were 50-80 A/cm^2. The subsequent heat treatment has allowed to increase j_c up 500-600 A/cm^2.

The ceramic samples of density 85-95% have been obtained by the explosive compacting with pressure 1500-4500 MPa. After additional treatment in air at 810-850^{O}C (20-40 h.) these samples had j_c ~1800-2000 A/cm^2. The optimal regimes of two stage sintering were developed for the samples, which were compacted by hydrostatic pressing (P~200-600 MPa). Using the two stage sintering gave the values of j_c ~1800 A/cm^2.

PHASE COMPOSITION, CRITICAL PARAMETERS OF THE Bi,Pb-2223 HIGH TEMPERATURE SUPERCONDUCTING OXIDES DEPENDING ON PREPARATION CONDITIONS, GAMMA-IRRADIATION

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The degradation of practical simple phase $Bi_{2-x}Pb_xSr_{2-y}Ca_{2+y}Cu_3O_z$; x= 0,2-0,4; y= 0-0,2 in dependence on temperature (550-810°C), partial oxygen pressure, gamma-irradiation were investigated by means of X-ray diffraction, inductance and resistance methods.

For our investigation the powders with volume of the superconducting (Meissner) phase c_m – 60-80%, the ceramics samples with T_c^o= 105-110 K and j_c(77 K, 0T)=1500-2000 A/cm^2 were used.

The superconducting phase $Bi_{2-x}Pb_xSr_2Ca_2Cu_3O_y$ (Bi,Pb-2223) with the highest critical temperature 105-110 K is not stable at temperatures between 500-800°C in air and oxygen. The highest speed of decomposition in air was observed at 750-770°C. The degradation rate in O_2 was higher at 3-5 times. The investigated phases were decomposed to the 2223 phase without or with small content of Pb and to the phase of the type $Pb_3(Sr,Ca)_5CuO_y$ and Ca_2CuO_3, 2212 and/or 2201. In nitrogen (P_{O2}=20 Pa) at temperatures of 550-750°C the superconducting characteristics decreased, the resistance increased during the first 20-40 minutes and they didn't practically change during the following 10-20 hours. On the X-ray diffraction, the phase composition didn't not change noticeably.

As a result of the $Bi_{2-x}Pb_xSr_2Ca_2Cu_3O_y$ decomposition at $P_{O2} \geq 10^3$ Pa the intergrain critical current decreased 10-20 times while the intragrain one increased 1,5-2 times. At $P_{O2}=10^1$-10^2 Pa the inter- and intragrain critical currents decreased by 5-10 times and by 1.5-2 times respectively as a result of oxygen extraction without visible destruction of the Bi,Pb-2223 structure.

It was shown, that the degradation rate of the critical parameters of Bi(Pb)-2223 ceramics under gamma-irradiation depended on the compound compositions and technological methods of their preparation. The speed of degradation affected by gamma-irradiation was increased in the presence of the impurity phases.

INVESTIGATION OF THE SOLID SOLUTIONS IN THE SYSTEMS $L_{2-x}Sr_xNiO_{4\pm\delta} - Sr_{1.7}Ce_{0.3}NiO_Z$ (x = 0; 1,0; 1,4)

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In this work the systems (1-y) $La_2NiO_{4\pm\delta}$ – (y) $Sr_{1.7}Ce_{0.3}NiO_z$ (A), (1-y) $LaSrNiO_4$ – (y) $Sr_{1.7}Ce_{0.3}NiO_z$ (B), (1-y) $La_{0.6}Sr_{1.4}NiO_{4-\delta}$ - (y) $Sr_{1.7}Ce_{0.3}NiO_{4-\delta}$ (C), (y=0-1.0; step – 0,15-0,2) were investigated.

The compositions of A, B, C systems were prepared by the standard ceramic technique from oxides and nitrates of the appropriate metals and from the fine compound and solid solution La_2NiO_4, $LaSrNiO_4$, $La_{0,6}Sr_{1,4}NiO_4$, $Sr_{1,7}Ce_{0,3}NiO_z$.powders. These complex oxides – the end members of systems – were previously synthesized by citrate method at comparatively low temperatures (750-950°C). The synthesis of compositions of system A was carried out in air, those of systems B and C – in an oxygen flow at temperatures of 1200-1250°C during 10-16 hours.

It was established that within the sensitivity limits of x-ray powder analysis in the investigated systems the continuous series of the solid solutions were formed. The physical-chemical properties of the final products were characterisized by thermal analysis (DTA, TG), x-ray diffraction, dilatometry, iodometry, conductivity, thermoelectric coefficient measurements.

The stability ranges of the solid solutions and end members of the systems were determined in air and oxygen. On the basis of analysis of temperature dependencies of conductivity, crystal parameters, relative linear extension, change of mass the presence of phase transitions and their types were determined.

It was shown, that temperature dependencies of conductivity of solid solutions of system A ($y \leq 0,5$) had the same character as La_2NiO_4 compound (semiconductor character of conductivity was up to 350°C, but above – metallic character). The specific resistance values of composition y=0,5 at 20°C (ρ) were $(1,2\text{-}1,5)\cdot10^{-2}$ Ohm·cm and they were in interval of the specific resistance values of La_2NiO_4 – $(1\text{-}2)\cdot10^{-2}$ Ohm·cm.

The solid solutions of C system ($y \leq 0,5$) had the same metallic character of conductivity at the temperature of liquid nitrogen up to ~ 400°C, as for $La_{0,6}Sr_{1,4}NiO_4$ and $Sr_{1,7}Ce_{0,3}NiO_z$. The specific resistance values for the composition y=0,5 were $(4\text{-}5)\cdot10^{-2}$ Ohm·cm, which are similar to ρ for compound $Sr_{1,7}Ce_{0,3}NiO_z$ ($Sr_{1,7}Ce_{0,3}NiO_z$ – ρ ~ $(2\text{-}5)\cdot10^{-2}$ Ohm·cm; $La_{0,6}Sr_{1,4}NiO_4$ – ρ ~ $6\cdot10^{-3}$ Ohm·cm).

INFLUENCE OF PRELIMINARY TREATMENT OF ULTRA-DISPERSE POWDERS ON MICRO-STRUCTURE AND PROPERTIES OF OXIDE CERAMICS

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Influence of preliminary thermal and ultra-sound treatment (UST) conditions of ultra-disperse powders (UDPs) on consolidation processes and properties of oxide ceramic materials is under investigation in the present work.

Objects of investigations were aluminium oxide UDPs of different dispersity (20-250 nm) produced by electric explosion of aluminium wire, hydrolysis of plate aluminium and plasma-chemical synthesis, and also theses powders after different kinds of treatment and experimental samples made of them produced by static and impulse compaction and the following sintering.

For increasing of technological characteristics of UDPs they were treated by different methods. UST was carried out in the USD-0,25 bath in ethyl alcohol, firing - at 450 and 650 °C during 1 hour, milling - in a planetary ball mill. It was planned that UST will help to mill big particles agglomerates and activate the following consolidation processes. Firing will promote dehydration and embrittlement of the powders. Milling in a planetary mill after thermal treatment was carried out to destroy agglomerates and hollow spherical particles.

Static compaction of powder was carried out at pressures of 80-500 MPa and impulse one - by high explosives in air within the pressures interval of 3-7 GPa. Samples were sintered in the HTF 12/15 resistance electric furnace in air within the temperature interval of 1300-1600 °C.

There were investigated physical-chemical properties of UDPs: initial and treated in different conditions. It was determined that the lowest filling density was for a plasma-chemical powder, which was, probably, stipulated by the particles shape (hollow spheres with diameter up to 250 nm and agglomerates of 1-3 mkm). UST in ethyl alcohol increased 1.4 times filling density of electric blasting powders, and 2.7 - of plasma-chemical ones.

Thermal treatment with the following milling influenced filling density in the same way as the UST. After the UST relative density of compactions increased 10-15 %. Density of sintered samples from powders treated with ultrasound increased 4-7 % depending on their type and microhardness - 25-33 %.

THE STABILIZATION of a STRUCTURE of CERAMIC MATERIALS, OBTAINED by a METHOD of a MICROWAVE of SYNTHESIS and SINTERING

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The outcomes of researches of action of a MICROWAVE of fields with frequency 2,45 GHz on ceramic materials with a structure perovskite and spinel on stages of synthesis and sintering are represented. The mathematical model of growth of a germ of a new phase under an operation of a variable exterior field is offered. Is shown, that in conditions of action of an exterior variable field the modification of direction of diffusion processes and conditions of a course solidphase of responses of synthesis happens. The kinetics of responses of synthesis is not described by the equations formal kineticses. The mode of introduction of the stabilizing components in an initial mixture of ceramic components by a method chemical precipitation of salts with restoring of the component up to metal is offered. A covering of particles of a material before synthesis thus is achieved uniform. At consequent kilning the metal envelope of particles oxiderated also happens introduction of the stabilizing component in a grain. Thus the stratum stabilizing a component will be derivated uniform. The outcomes of a research of physical properties of obtained ceramic materials are represented. Is shown, that in a case ferroelectrics with a stratified structure possessing in high temperature of a Curie it is possible to achieve conditions of formation of barrier stratums reducing along with the stabilization a structures in emerging of semiconducting properties. For spinel of structures because of ferrite of a triple system copper-nickel–zinc obtains materials with a fine-grained structure. The conditions of synthesis ferrite ceramics are defined. The high-frequency properties are investigated and is shown, that the sintering in a MICROWAVE fields reduces in formation of a homogeneous grain structure, suppresses processes second recristallization. The composite ceramic materials because of multicomponent oxide of systems are obtained. The method of selective restoring of separate components in the process обжига creates metal ceramics a structure possessing high mechanical properties. Kilning of three-component systems because of oxide of iron, aluminum and zirconium has allowed to achieve a mechanical impedance on 30 % exceeding an impedance of ceramics from pure oxide of aluminum. The obtained materials are characterized high abrazive by properties and mechanical durability.

WATER–THINNABLE POLYMERIC BINDERS IN TAPE CASTING AND DIE PRESSING OF ALUMINA

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Various water-soluble binders and plasticizers are now being used in the ceramics technology for different forming methods. However, this type of binders not always fulfills our expectations, exhibits low mechanical strength (in the case of profiles obtained by pressing) and low flexibility.

Due to the small number of available water-thinnable binders, studies have been undertaken on the application in the ceramics technology of specially synthesized acrylic-styren, polyurethane and vinyl acetate copolymers with a built in internal plasticizer.

Copolymers of vinyl acetate and allyl ethers of alkoxypolyoxyethylene alcohols were used in the studies. The introduction of hydrophilic poly(oxyethylene) chains as side groups was the purpose of the copolymerization of vinyl acetate with these ethers. The hydrophilic poly(oxyethylene) chains bearing surfactant properties were to assure stability of the emulsion without an additional polymer or surfactant, and also to assure an improvement of the wettability of the ceramic powder.

The copolymers synthesized were applied for the forming of Al_2O_3 by tape casting and uniaxial pressing. The effect of the type of copolymer on the rheological properties of the powders pressed (thickening ability), apparent density, mechanical strength, both before and after sintering, have been studied.

After sintering at 1650 °C/1h profiles of relative density >97%, open porosity <1%, bending strength 300-500 MPa and of Weibull's modulus 8-10, were obtained.

SECTION C. STRUCTURAL CERAMICS: PROPERTIES; INDUSTRIAL APPLICATION **111-140**

THE REINFORCED CERAMIC STRUCTURES OF MAXIMAL CRACKRESISTANCE

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In many areas of modern mechanical engineering, aviation and space engineering, in shipbuilding, engine and chemical devices are widely used composite ceramic products such as the reinforced layered structures or layered structures with protective ceramic coverings. In connection with essential fragility of ceramic materials the main criterion of efficiency of use of ceramic products for crucial constructive elements is them crackresistance. In the report as applied to thin-walled structures such as plates, panels and shells the approach by definition maximal crackresistance is developed. Thus are considered the quasihomogeneous polyreinforced ceramic-metal structures and structures with unilateral and bilateral ceramic coverings. Structures of reinforcing and the structures of ceramic coverings providing maximal crackresistance are determined. The structures working in a normal temperature mode and in conditions of high and low temperatures are considered. Ways of improvement of ceramic products are investigated at influence on them of explosive and shock loadings.

RATIONAL DESIGNING THE CONSTRUCTION OF CERAMIC COMPOSITION OF LAYERED STRUCTURE WITH REINFORCING MEMBERS

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The constructional ceramics includes the large group of ceramic materials, used for creation the constructions and details carrying static, dynamic and cyclic loadings. One of perspective directions is use of layered metal-ceramics with ceramic reinforcing members in the constructions using at high temperatures, for example, disks and vanes of gas turbines.

In this case main problem is the reliability at operation, so far as ceramic materials are fragile. Therefore it is necessary to pay special attention to the problems of the strength of the constructions of ceramics of such type.

The method of designing of layered-fibrous design with equalstrength binding material and equalstress reinforcing members is offered. The essence of a method consists that for the given conditions of temperature and force influence on a design the geometrical parameters of a designs ensuring a condition of equalstrength binding material and equalstress reinforcing members are determined. The required geometrical parameters of a design include intensity and direction of stacking reinforcing members and thickness of layers binding. The equalstrength state binding material is the such stress-strain state, when the maximum quantity of volume binding material is on a marginal level of a stress with given factor of a stock on strength, and nowhere this level is not exceeded. Besides geometrical parameters of a rational design the method allows to determine to the most favorable initial stress-strain state, which is formed at manufacturing, and to put forward the technological recommendations for its creation. For typical constructive elements the examples equalstrength of the projects of designs with equalstress reinforcing members are constructed.

On an example of accounts of rotating disks is shown, that use of metal-ceramic disks of layered-fibrous structure allows to raise efficiency of disks at the expense of increase of working temperatures and essentially to lower weight of designs.

SiCN NANOCOMPOSITE : PROCESSING AND CREEP BEHAVIOUR

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A Si_3N_4/SiC nanocomposite which presents a high ductility has been developed. The starting powder was a nanometric silicon carbonitride powder synthesised by laser pyrolysis from a liquid precursor : hexamethydisilazane (HMDS). The C/N ratio (= 0.2) was controlled by the introduction of ammonia into the reagent mixture during the synthesis. A dense (98%) and homogeneous material was successfully obtained by hot-pressing with 6 wt% yttria and 3 wt% alumina as sintering aids. The microstructure of the as-sintered material consists of pockets of nanosized (200 nm) equiaxed β-Si_3N_4 grains surrounded by elongated Si_2N_2O grains embedded in a glassy phase.

The creep behaviour was studied under compressive loading in air. The results were analysed using the semi-empirical Norton -Arrhenius equation :

$\dot{\varepsilon} = A\sigma^n \exp -E_a/RT$, where $\dot{\varepsilon}$ is the strain rate, A is a constant, σ is the stress, n is the stress exponent, E_a is the apparent activation enthalpy, R is the gas constant and T is the absolute temperature. Using a stress- jump experiment at 1200°C with stresses ranging from 30 to 180 MPa the stress exponent was determined to be equal to 1. The apparent activation enthalpy (E_a = 680 kJ/mol) was derived from a temperature step experiment between 1200 and 1350°C under a stress of 45 MPa. Additional isothermal creep tests were carried out at 1350°C under 45 and 180 MPa. The results were compared which whose obtained for a superplastic silicon nitride used as a reference[1]. The ductility of the nanocomposite is very high. For instance, at 1350°C and 45 MPa, the true strain of the nanocomposite is one order of magnitude greater than that of the reference (after 20 h, ε = 30% instead of 3%). From these results, it is hoped that this new silicon nitride based material will allowed near-net shape forming of complex parts at rather low temperatures and high strain rates.

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EFFECT OF STRUCTURAL ANISOTROPY ON STRENGTH OF CERAMIC COATINGS

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The effect of grain morphological anisotropy and crystal axial texture on the strength properties of ceramic coatings was studied. The coarse grained boride (FeB, Fe_2B) coatings consisted of columnar crystals as well as the fine grained nitride (TiN_x) and carbides (TiC, VC, NbC) coatings consisted of laminated or globular crystals were used. Coating strength was evaluated by the HV and K_{Ic} values determined in tests with indentation. The degree of grain anisotropy was assessed by the coefficient of grain form determined like ratio of linear dimension of short axis to that for long one ($k_f = D_{min}/D_{max}$). Axial crystal texture was defined by pole density P_{hkl} determined by means of XRD analysis.

Essential anisotropy of coating resistance to fracture occurred in response to anisotropy of coarse columnar crystals and fine laminated grains was found. The following relationship of the fracture toughness criteria is revealed: $K_{Ic}(\pi/2) > K_{Ic}(0)$ (where symbols $\pi/2$ and 0 are gained to the K_{Ic} values determined in coating cross section perpendicular and parallel to surface). As far as the axial texture [001] is formed in boride columnar grains the fracture anisotropy is reduced with the increasing of texture perfection due to the $K_{Ic}(\pi/2)$ value decreases sharply unlike that the $K_{Ic}(0)$ value remains constant. The equality of the fracture toughness values such as $K_{Ic}(\pi/2) = K_{Ic}(0)$ is found to be with $P_{002} \geq 2.5$.

Increasing the $K_{Ic}(0)$ value was revealed in fine grained coatings at the spheroidization of grains in the range $0.3 < K_f < 0.5$. The $K_{Ic}(0)$ values such as K_{Ic}^{min} and K_{Ic}^{max} determined in the proper ranges such as $K_f \leq 0.3$ and $0.5 \leq K_f \leq 1.0$ are found to be invariant. The relationship of the $K_{Ic}(0)$ criterion extreme values is found to be like the constant number $K_{Ic}^{max}/K_{Ic}^{min} \cong \sqrt{2}$ regardless to coating composition.

As applied to coatings which are characterised by FCC lattice-like NaCl the increasing of the $K_{Ic}(0)$ value up to 50% caused by the modification of the axial texture type from [100] to [111] being accompanied by consequent increasing the perfection of last one was found.

Generally at the same composition of coatings the HV values is found to be invariant with modification of grain shape or axial texture.

THE CIP TECHNOLOGY FOR CERAMIC PARTS PRODUCTION

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Modern processes provide manufacture of ceramic powders with particle size from 20 to 200 nm. This ensures high performance of the sintered ceramics. However utilization of such powders in conventional ceramic technologies is complicated. Cold isostatic pressing (CIP) is one of advanced methods just enabling to work with such ultrafine powders. The present work is devoted to description of ceramic parts production technology using CIP.

According to the CIP technology developed compacts have to be manufactured by way of CIP in rubber/metal pressforms at pressures below 0.2 GPa. The pressure value is to be chosen based on necessity of green machining to eliminate the surface imperfections arising from elastic envelopes in the compacts. Green strength at such pressures is proved to be sufficient for rough green machining but precludes accomplishment fine details (turnings, facets, edges etc.) due to cleavages or chipping.

Implementation of metal in CIP pressforms improves performance of the compacts, lowers losses of the powder, but causes some uneven density distribution. Subsequent additional CIP route in elastic envelopes makes the distribution more even, CIP pressure value being chosen based on the highest strength of sintered ceramics.

Such compacts have higher strength but are hardly workable too due to their brittleness. To overcome this shortcoming, the compacts would be subjected to low temperature annealing providing relaxation of residual stresses and strengthening of bonds between structural elements of the powder. As a result, annealed material has good workability. It enables green machining of the compacts to the right dimensions with acoount of shrinkages during sintering.

Low temperature annealing does not affect on sintered properties and sintering regime. Dimensional accuracy of the sintered bodies corresponds to 12th Class of Accuracy and needs in further finishing routes.

The present technology have been used to manufacture ceramics elements of dies, friction bearings, and valves from zirconia or alumina powders.

ROOM DEGRADATION OF SOME GRADES OF PSZ

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Degradation of metastable PSZ based materials is now extensively studied, generally at elevated temperatures, in view of possible wide implementation. Room ageing of such materials during storage of the sintered ceramics is of great scientific and especially practical interest. Unfortunately, such experiments require long times to be made and only few publications are known dealt with PSZ room ageing in neutral environments, where degradation term was determined to be within 4 to 10 months [1].

Present work is devoted to studying the room degradation in a number of ceramics ZrO_2 + 3 mol.% Y_2O_3. Ceramic specimens had been stored in as-sintered condition and subjected to grinding immediately before standard mechanical testing. Results are presented in Table 1.

Table 1. Degradation of Y-PSZ due to room ageing

Y-PSZ Grade	Grain size, μm	Ageing, months	Initial props			Degraded props		
			ρ, g/cm³	K_{1c}, MN/m$^{3/2}$	σ_b, MPa	ρ, g/cm³	K_{1c}, MN/m$^{3/2}$	σ_b, MPa
Nilcra, Australia	15	38,5	6,12	8,2	896	6,10	4,0	1030
Tosoh, Japan	1	38,5	6,13	7,9	669	6,17	2,3	670
Hydrothermal, IPMS	15	38,5	5,93	7,9	587	6,07	3,2	839
Coprecipitated, VSMMK	20	22,3	5,97	8,7	572	5,97	3,3	410
Self-reinforced	0,5	22,3	5,96	10,0	656	5,91	8,3	370

Values of ρ and σ_b are constant within scattering limits indicating on negligible changes in phase composition and dominant role of the renewed surface layer. The data on fracture toughness are of most importance since (i) just high values of K_{1c} make the ceramic tough and (ii) it is most sensitive to structure. It is seen that K_{1c} drops in fact up to level of a monoclinic ZrO_2 in the course of three-year storage for all grades of PSZ excluding self-reinforced one. It is worth to note that the storage degradation term for ceramics brought to a stability threshold can be as short as few weeks.

As a conclusion, conventional PSZ based materials would be used in conditions precluding their long-term storage while self-reinforced ceramics which are more proof against other degradation environments as well [2] can find much more wide use.

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THE INFLUENCE OF CIP PRESSURE AND SINTERING TEMPERATURE ON PROPERTIES OF CERAMICS IN SYSTEM ZrO_2 – 3 mol. % Y_2O_3

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Ceramics specimens were manufactured using cold isostatic pressing (CIP) at pressures up to 0.8 GPa and air sintering with isothermal stage from 1400 °C to 1620 °C from laboratory-made powders ZrO_2 - 3 mol. % Y_2O_3 obtained by way of co-precipitation hydroxides from aqueous chloride solutions by aqua ammonia with subsequent calcination at 850 °C. Sintered specimens were used to measure hydrostatic density and three-point bending strength.

It is found that the sintered density monotone increases with rising both CIP pressure and isothermal stage temperature. Sintered density had increased from 4.0 g/cm^3 at 0.1 GPa to 5.2 g/cm^3 at 0.8 GPa at the temperature 1400 °C; from 4.7 to 5.7 g/cm^3 at the temperature 1550 °C; and from 5.5 to 5.8 g/cm^3 at the temperature 1620 °C. The strength of ceramics had varied in general accordance with the density from 200 MPa (density 4.0 g/cm^3) to 900 MPa (density 5.8 g/cm^3).

An experiment on artificial re-granulation of the powder was carried out as well. Re-granulation was performed by way of treatment of initial powder in laboratory planetary mill in hard regime (270 rpm). Obtained powder was used to produce ceramic specimens at CIP up to 0.8 GPa and sintering with isothermal stage temperature 1500 °C. This lot has shown almost total independence of density and strength on CIP pressure and demonstrated the best properties, the density being within 5.90 to 5.95 g/cm^3, the strength within 750 to 930 MPa.

INVESTIGATION OF THE NONLINEAR STRESS – STRAIN STATE OF A LAMINATED CERAMIC COMPOSITE

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Experimental investigation of the mechanical response of a model laminated ceramic composite was conducted under ambient conditions. The composite was a package of twelve alternating TiB_2–B_4C and SiC layers stacked together (the SiC layers were of relative porosity up to 40 %). It was produced by slip casting of thin films followed by their rolling and cutting in billets, then packing the billets in the form of alternating layers and hot pressing the package. After the composite had been fabricated the microcracks were observed in its layers. A beam-like composite specimen of size $3\times6\times45$ mm^3 was subjected to bending at the deformation rate of 0.005 mm/min. On the basis of the experimental "load (F) – deflection (w)" curve (fig. 1, a) and *a priori* estimated values of elastic moduli for composite layers the generalized nonlinear "stress (σ) – strain (ε)" curve (fig. 1, b) for a specimen material as a quasi homogeneous structure and the similar curves for the materials of layers formed the composite were constructed. They correspond to the loads at which a continuity of the "F – w" curve remain. The data obtained allowed the stress – strain state of the composite concerned to be investigated in theory. In particular, the maximum values of the normal stresses in the specimen calculated using the nonlinear approach were demonstrated to be lower than those obtained on the linear one.

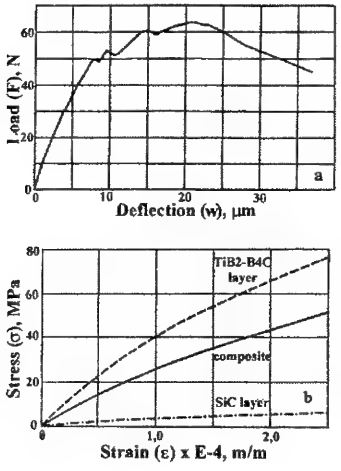

Fig. 1

PRODUCTION AND PROPERTIES OF NOVEL CARBIDE/METAL SKELETON COMPOSITES

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It is well known that a combination of properties typical of carbide ceramics and metals in one material may provide a composite with superiority over other materials. Properties of common carbide/metal phase matrix composites, i.e. metals reinforced by particles of refractory carbides, are mainly determined by the properties of the metal phase. Thus, resulting in significant deterioration of their properties at high temperatures. Products made from such materials cannot be used at temperatures greater than softening point of the metal.

The present study was aimed to develop new preparation methods for production of carbide/metal composite materials with high temperature resistance. Thus, keeping their service ability even at extreme conditions, such as temperatures greater than melting point of the metal. The developed methods are based on the use of "near net-shape" forming technology in which the size and shape of articles are determined and these are kept unchanged during the reaction sintering process. This results in a fully dense body with the required shape and phase composition.

The new preparation technique has been proven in a series of new skeleton composites: Cr_3C_2/Cu; TiC/Cu; TiC/Al; B_4C/Al; TiC/TiNi, etc. Two three-dimensional interpenetrating skeletons build up the microstructure of the prepared materials: carbide and metal phases with typical sizes of the structural elements being a few to several microns. In addition, it is possible to vary the relative volume part of both components in wide ranges.

The prepared materials have good mechanical properties: Young's modulus of up to 200 GPa, bending strength of 400-1000 MPa, hardness of up to 60 HRC in combination with good thermal and electrical conductivity and small thermal expansion coefficient. The materials have advantageous properties at high temperatures, especially.

The study includes very positive results from application tests using the prepared skeleton composite materials in electrical and tribotechnical devices.

FIBROUS INGREDIENTS –A NEW APPROACH TO THE DEVELOPMENT OF SI_3N_4 MATERIALS

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It is shown in this paper that the use of the ingredients with fine-fibered microstructure in order to improve physical and mechanical properties of ceramics is promising.

Silicon nitride with 90% of α-phase obtained by self-propagating high-temperature synthesis (SPHTS) was used as a matrix. The process optimization relative to burning temperature, nitrogen pressure, silicon particle dimensions, charge composition and other parameters makes possible a high and low temperature synthesis of silicon nitride with different characteristics in an industrial reactor.

Microfibers 0.1-1.0 μm in diameter and 15 μm in length cause self-reinforcement of ceramics through the formation of needle grains with high length/diameter ratio.

The use of sintering promoter in the form of $Al_2O_3 \cdot H_2O$ aerogel microfibers (filaments with diameter 20-100 nm and specific surface up to 800 m^2/g) is already profitable when the content is 0.5-1 mass.%. It manifests itself in the improvement of ceramics physical and mechanical properties, namely, in the attainment of theoretical density, half as much again strength including high-temperature strength, increase in oxidation resistance and operating temperature (up to 1300°C).

Introduction of long and short whiskers of SiC_w and Si_3N_{4w} in Si_3N_4 (SPHTS)-$Al_2O_3 \cdot H_2O$ system tends to increase crack and heat resistance.

RESEARCH OF PATTERN AND PHYSICAL-MECHANICAL PROPERTIES OF A POWDERED COMPOSITION ON THE BASIS OF CUPRUM CONTAINING - Si_3N_4 AND BK8

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This research investigates structural and physicomechanical performances of a powdered composition: Cu - Si_3N_4 - BK8 - C. In makeup of a powdered composition base weight percent of charge is compounded by(with) electrolytic cuprum with the size of fragments 100 microns, and also dispersed ceramic and hard-alloy fragments (silicon nitride Si_3N_4, hard alloy BK8), graphite. Gravity of a powdered mixture of 7,5 g /cm^3.

Makeup of a powdered composition chose from reasons of making of a hull of a product from a tenacious material with presence of dispersed members of high hardness, which one maintain source indexs physicomechanical performances at high temperatures - 1000° C.

In operation have utilized a powder of silicon nitride containing fragments and phases: α - Si_3N_4 (30 %) and β - Si_3N_4 (70 %). A powder of hard alloy - BK8 have gained on the standard know-how. The mean size compounds 2 microns. A X-ray spectral analysis and the metallurgical surveys of obtained makeups have shown presence of phases and actuations describing makeup of a material. The lack of intersolubility of members of a powdered composition after caking with conservation of the source performances of a material is determined.

Cohesive strength and tearproof characteristics of sintered and not sintered compound compacts from a powder composition Cu - Si_3N_4 - BK8 - C. Fracturegraphical studies have shown that the basis of a framework (of compact and sintered material) of powdered composition Cu - Si_3N_4 - BK8 - C is compounded with copper ramified fragment (with the small floor space of interparticle contact). The solid dispersed fragments, in view of lack(absence) of intersolubility and small size of fragments (2 microns), are laied out inside a copper hull of a product.

Thus, the analysis of properties of the designed powdered composition Cu - Si_3N_4 - BK8 - C, has allowed to fix, base performances of a material of shockwaves, conserved under operating.

AlN BASE CERAMICS CONTAINING TiN, TiC, TiB_2

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High chemical inertness and thermal conductivity of AlN makes this compound attractive for high-temperature applications as a material for wear- and thermal-resistant parts. However, achieved level of mechanical properties generates a need for increasing strength and fracture toughness of AlN ceramics. Generally, to improve mechanical characteristics of ceramic materials, strengthening elements of second phase are incorporating into the matrix [1]. Second phase inclusions increase fracture toughness of the ceramic material dissipating the crack energy. These elements of structure may have a shape of particles, whiskers or plates. The strengthening can be realized by several processes: first, additional element of the structure deflects or blocks the crack; second, the element of metal phase forms a bridge absorbing the energy of the crack under plastic deformation; third, the propagating crack can be stopped when the element of second phase undergoes a phase transition in conjunction with a volume expansion initiated by the stress field of the crack.

Such refractory compounds as titanium carbide, titanium nitride and titanium diboride were added to AlN ceramics to improve the mechanical .behavior of the material. The samples have been prepared by conventional powder processing, i.e. by homogenization of the powder mixtures in the planetary mill, uniaxial cold pressing and pressureless sintering in nitrogen in the 1800-1850 °C temperature range. The final densities and some properties of the AlN base composite samples are presented in the Table.

Table. Composition (wt%) and properties of AlN base samples.

Composition	Theoretical density, g cm^{-3}	Relative density, %	HV 0.5, GPa	Thermal conductivity, W m^{-1} K^{-1}
AlN(Y_2O_3)	3.30	99	9.5±1.1	137
AlN(Y_2O_3) + 25% TiN	3.65	99	11.1±1.6	87
AlN(Y_2O_3) + 20% TiC	3.54	98	12.6±0.6	73
AlN(Y_2O_3) + 20% TiB_2	3.49	92	10.5±0.6	n.m.
AlN(Y_2O_3) + 10%TiN + 10% TiB_2	3.57	95	11.8±0.8	n.m.
AlN(Y_2O_3) + 10%TiC + 10% TiB_2	3.52	94	11.4±0.3	n.m.

The final densities of the AlN/TiN and AlN/TiC samples exceed 98.0% of the theoretical value. The densities of the TiB_2 containing samples are somewhat lower and were measured to be 92.0-95.0% of the theoretical value. Nevertheless, the Vickers hardness HV 0.5 of the composite samples is higher than that of AlN ceramics. The Vickers hardness of the samples containing titanium carbide was measured to be 12.6 GPa.

The high-density composites, pressureless sintered from commercial aluminum nitride, titanium carbide, titanium nitride and titanium diboride powders, show improved hardness in comparison to AlN ceramics retaining its high thermal conductivity. The pressureless sintering processing route makes possible to manufacture parts of complex shape from AlN base ceramics containing hard materials.

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CRACK-RESISTING CONSTRUCTION MATERIALS AND COMPLICATED CONFIGURATION WARE OF MECHANOACTIVATED POWDERS OF OXYGEN-FREE COMPOUNDS

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The creation of construction materials having a complex of given properties and structures is possible under the provision of hardphase reactions on nano-level in technologies. Sol-gel process and mechanochemical methods of hardphase reaction intensification found its application in the development of up-to-date technology of structural ceramics based on oxygen-free compound powders, primarily SiC, B_4C, Si_3N_4 at NTU (KhPI). Combining the method of non-organic and organic chemistry has enabled the creation of high quality construction materials on the basis of refractory compounds of less than 1 mkm. It has been proved that using hetero-organic substances the process of mechano-activation of hardphase reaction is observed in the first place as a result of active areas created at the newly-formed powder surfaces of high faulted grates of fine pounded powders (SiC, Al_2O_3, B_4C, Si_3N_4 etc.), the creation of carbon clatrate in SiO_2 etc. Sol-gel process, the elements of which are used in the developed technologies assists in the introduction of superdispersed components into charge that are also used under the synthesis of the given structure of nano-sized new formations. A low-temperature synthesis β-SiC and other compounds have been determined.

The regulation of the ratio of composition-structure-property allows for the creation of high-strength and crack-resisting construction materials. Using modified powders and the method of hot-pressing the construction materials containing $K_{1C} \geq 6,5$; 5,8 and 5,1 $MPa \cdot m^{0,5}$ from SiC (B_4C), Si_3N_4 and Al_2O_3 correspondingly have been developed. The technologies of complicated configuration of modified powders Si_3N_4, B_4C, Al2O3, SiC have been introduced. Hydrostatic reduction allows bringing the porosity of the specimen to 0-5 %, and firing in the given medium, reactional agglomeration and siliconized results in thin-walled ware having high performance of physico-mechanical properties. Big-sized ware of complicated configuration on the basis of all the listed refractory compounds might be of interest, but it is the given configuration ware of SiC or B_4C as well as big-sized ware of Si_3N_4 and Al_2O_3 of low thickness that are the most attractive.

NANOSTRUCTURED BORIDE/NITRIDE FILMS

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Numerous studies of high-melting point compounds such as TiN, TiB_2, TiC, AlN, Si_3N_4, and some other with the melting point above 2000°C which can be described as advanced ceramics is connected with the creating of new generation of materials. Their promising properties and wide spread application as diffusion barriers in microelectronics, hard wear resistant coatings on cutting tools, or as a corrosion and abrasion resistant layers on optical and mechanical components are well known. An additional interest is connected with the study of the corresponding nanostructured films and coatings which mechanical, physical-chemical, and electrical properties because of very small grain size can be differ significantly from the properties of the materials in usual crystalline state.

In our work are presented the results of investigation of the physical-chemical and physical-mechanical properties as well as the thermal stability of thin nanostructured boride/nitride films.

The films of TiN, TiB_2, Ti(B,N), AlN, (Al,Ti)N, (Al,Ti)(B,N), and (Al,Ti,Si)(B,N) with a thickness about 1-3 μm on Si, glass-ceramic, stainless steel, and TiB_2 single crystal substrates were prepared by magnetron non-reactive sputtering. The film composition and structure were characterized by XRD, TEM, SAED, HREM, AFM, and AES. According obtained results all prepared films are characterized as an objects with very fine nanostructure (crystallite size 3-30 nm). Hardness measurements were performed using both a Vickers microhardness tester and NanoIndenterTM II device with the triangular Berkovich diamond indenter. The electrical resistivity was studied by the four-probe method; the elastic properties were characterized by means of nanoindentation test and the acoustic method. Annealing of the films at temperatures 700°C and 1000°C was carried out at residual pressure about 10^{-4} Pa.

The influence of sputtering regimes (radio frequency, constant current, and constant current with the different bios voltage on substrates) as well as the substrate temperature on structure, morphology and properties of nanostructured boride/nitride films are discussed in detail. Essential attention was focused on the investigation of the crystallite sizes and size effect.

CARBIDE FOAMS – CHEMICAL REACTIONS CATALYSTS

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The catalytic activity of titanium carbide foams in a common observation. However, it's direct effective use has not been observed, for foam carbide in melted and blended state is not used as a catalyst. But in its powder state it is characterized by not very high specific surface and not so high gas permeability, strength that prevent them of being excellent effective catalysts.

The aim of this work is to create new carbide foams of various chemical composition with controllable properties, to produce penowares of any size and shape. The production technique of carbide foams includes the mixing of microspheres from phenoloformaldehyde resins as well as carbon and cresospheres (thermal power stations rejects) with the liquid carbonific bender and carbide forming compound (titanium powder or its oxide). Subsequent treatment enables to produce carbide foams.

The developed porous material retains all valuable properties, characteristic of titanium carbide, bat in the same time it has high open porosity, specific surface, heat resistance, corrosion resistance, gas permeability, structural strength. But it possess low density, flammability and heat conductivity.

Technical properties of titanium carbide

Open porosity	50 – 98
Average size of structural pose cell, mm	0,1 … 0,4
Density, g/sm^3	0,1 … 1,8
Specific surface, m^2/g	0,1 … 10
Compression strength, Mpa	up to 30
Specific heat conductivity, Vt/m·K	0,1 … 0,5
Electro conductivity, Om^{-1}·m^{-1}	1,0 … 10^4

The developed materials can find their application as block components of catalyst carries operating at elevated temperature.

MICROSTRUCTURE AND PHASE COMPOSITION AFTER HOT DEFORMATION OF THE EUTECTOIDALLY DECOMPOSED ZrO_2-MgO STRUCTURAL CERAMICS

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The ZrO_2 based ceramics belongs to the high toughness ceramics, in which precise knowledge of the relation between processing and the path of phase formation sequences is essential to provide a sufficient fracture resistance [1]. As it is known the sub-eutectoid heat treatment decreases the stability of tetragonal ZrO_2 [2], so in the previous paper the study of microstructure and decomposition mechanism was undertaken [3].

In the present paper the results of investigation of Mg-PSZ structural ceramics with 11,5 and 13 mol.% MgO, after eutectoid decomposition and hot compression are presented. The X-ray phase analysis, analytical transmission electron microscopy and scanning electron microscopy have been applied to study their phase composition and structure.

Compacts of powders were sintered at 1500°C and slowly cooled. It was found that eutectoid decomposition took part during cooling, predominantly leading to the formation of tetragonal ZrO_2 and cubic MgO phases. In the further stage of transformation also large amount of monoclinic ZrO_2, in the form of internally twinned particles was formed, whereas part of the material remained cubic ZrO_2 – MgO solid solution.

A compression test was performed at 900°C at the rate $10^{-5}\ ^1/_s$. Samples were compressed up to 10%, giving as a result deformation bands and discontinuous recrystallization, with the recrystallization front overlapping the boundaries of the cells of eutectoid precipitates. The products of the eutectoid decomposition undergo rafination in the sample plastically deformed in comparison with not deformed one. Moreover the amount of the monoclinic ZrO_2 phase, both in the matrix and in the precipitates increased. The monoclinic phase formed due to deformation by martensitic mechanism, often inside or between ZrO_2 precipitates in the matrix.

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NONFIRED REFRACTORY COMPOSITES ON POLYMER BASE

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During last years the role of the nonfired refractory materials in the steelmaking industry is abruptly increased. This materials contain as binding agent a polymer systems on the base of reactive oligomers. Development of this direction is caused by some advantages such materials in comparison with traditional materials. Presence of the polymeric binding agent in the refractory material strengthen the fresh-molded samples, facilitating the transportation of intermediate material between production operations and allowing to manufacture the refractory production with high structural strength after thermal treatment. Use of the nonfired refractory ware and ramming mixture leads also to considerable energy saving. Both thermoplastic polymeric materials (with coke no more than 5 %) and heat-resistant thermoreactive polymeric systems which provide strengthening of the three-dimensional structure are used and the their choice is depends on the service conditions of refractory ware and its functional area.

To provide stability of the nonfired refractory products under melt metals and slag in open-hearth furnace and other heat units the furan-epoxy polymeric systems (FEPS) are proposed to be used. FEPS is the product of the thermomechanical combination of furfurol-acetone monomer FAM or FA and epoxidianic oligomers.

- FEPS has high fluidity and this property allows to provide more regular distribution of the binding agent in the bulk of the composite;
- furan epoxy polymers have the high solid pyrolytic residue after thermal and thermal-oxidative breakdown (under inert and oxidative media respectively). It allows to obtain nonfired refractory material which do not loose structural strength after exposition under high temperature, metal and slag melt;
- high wetting ability of FEPS to basic components of refractory furnace charge. It gives the durable adhesive contact on the interface surface "plastic binder - dispersed refractory filler". Due to the good wetting the compounds with minimum structural defects in the interfacial phase can be made and it leads to increase of static compression and flexural strength of refractory;
- polymers of this class have practically unlimited resources in present-day and in future. The main source of basic component of FESP - furfurol-acetone monomer FAM - is renewable natural resources (heels of maize, cotton-plant, saw dust, other pentozan bearing products).

So, use of furan-epoxy monomer-oligomeric compositions as a matrix for refractory allows to obtain the products with complex high strength, processing characteristics and running ability. The structure of composite has minimum amount of structural defects and this fact provide high level of operate reliability.

GRAIN SIZE DISTRIBUTION IN ZIRCONIUM OXIDE - MULLITE NANOCERAMICS

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The size distributions of grains of tetragonal zirconium oxide and mullite in zirconium oxide-mullite nanoceramics containing 20 and 30 wt% of zircomium oxide were determined. The technique of measurement and calculations of the grain size distribution by the X-ray line profile has been used. A ceramic composite material with matrix (mullite) grain sizes of 30-160 nm and toughening phase (tetragonal zirconium oxide) grain size of 10-28 nm was manufactured by the method of hot pressing the amorphous oxide granuls.

It was found that size grain distributions, both of mullite and tetragonal zirconium oxide, look as "steps". The distribution form does not depend neither on the composite content nor on the parameters of hot pressing and is determined by the stability of conditions during crystallization (temperature and content of amorphous material), the grain growth rates and nucleation rates being constant. The height of a "step" is proportional to the nucleation rate, and the width of a "step' (limited grain size) - to the grain growth rate.

The form of the grain size distribution measured and calculated by the X-ray line profile, for zirconium oxide-mullite ceramics, coincides with that of the distribution constructed by a theoretical-calculation consideration of the concurent crystallization of two phases in the amorphous material.

The grain size distribution as "steps" is characteristic for nanoceramics obtained by compactization and crystallization of amorphous material, unlike the materials sintered of crystalline powders in which the grain size distribution has a bell-like form.

RESEARCH OF A FEASIBILITY IN SUBMERGED ELECTRIC MOTORS OF PARTS OBTAINED A POWDER METALLURGICAL TECHNIQUE

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The powder composite materials distinguish valuable advantages, namely capability of obtaining and regulation of different performances. Rational guard ropes of a material and production process enables to receive parts of heightened reliability, minimum mass and low-level cost, that is characteristic for parts and units SEM.

The submerged electric motor (SEM) is the particular unique machine (at an external diameter of a body 103, 117, 123 mms length reach 6-18 m). A high frequency of rotation - 50 s^{-1}, major pressure - up to $200 \cdot 10^5$ Pa, the operation conditions in a slit (temperature up to 110^0C, depth - up to 2000 m), where the direct maintenance behind it is impossible, present heightened requests to use reliability SEM.

Are conducted theoretical and experimental researches of a feasibility of parts SEM, made a powder metallurgical technique, the powdered materials for them are selected, the methods of manufacturing of parts and conduct SEM, under operating conditions on crafts are studied.

The researches have shown, that parts made a powder metallurgical technique for SEM (turbine and a bore protector of a material ЖГр1, bearing case from a material ПТХ4-2 [1] and support from a material ДО4Ц4Гр2Мс3Б [2,3]) answer presented requests and are recommended to operation.

The perspective application of items made of the set forth above materials, has allowed to save raw material, semifinished items and specially, that is very important, to lower the costs of manufacturing of parts SEM at simultaneous preservation of the main figure of merits and reliability of electric motors.

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INTRICATELY-PROFILED CERAMIC CONSTRUCTIONS BRAZED WITH OXIDE SOLDERS FOR DIFFERENT BRANCHES OF SCIENCE AND ENGINEERING

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The development of an accelerating and laser engineering as well as the works in the field of the plasma physics and instrument engineering brought forward a task for the manufacture of large sized ceramic constructions of intricate configuration with high thermomechanical properties. In a number of cases their manufacture by means of standard technologies employment does not seem to be possible.

In the open joint-stock company "Ukrainian research institute of refractories named after A.S. Berezhnoy" the technological processes for the manufacture of ceramic products on the basis of ultradense corundum ceramics containing not lesser than 99,5 % of Al_2O_3 were developed. Such ceramics possesses high mechanical ($\sigma_{bending}$ 250–280 MPa) and dielectric ($E_{strength}$ 18–20 kV/mm) properties. Furthermore it contaminates up to minimum the working volumes at an action of heat flows with a power of 1–3 d/cm^2 and the bombardment of the surface materials by hot ions.

The laid down task is solved by jointing more simples elements into intricately profiled large-sized constructions by means of their brazing with hightemperature oxide solders. A number of solders using Al_2O_3–SiO_2–MeO (MeO–CaO, BaO, MgO) system with a melting point from 1200 °C up to 1500 °C as well as the configuration of brazed surfaces was developed. For their manufacturing the profile mechanical treatment of the ceramics by diamond instrument including the polish of internal and external surfaces in different planes was developed as well.

The carried out developments allowed to produce brazed radial elements with a section of 100×100 mm with a length of 800 mm, different ceramic constructions of variable section and to proceed to the manufacture of section assemblies with diameter of 140 mm and length of 1200 mm.

Brazed constructions ensure the vacuum up to 1.10^{-12} mm mercury gauge without a seal failure up to 1500 °C.

In accordance with a developed technology the products for technological eximer lasers used in the microtreatment of different surfaces of high hardness in systems of an input of charged particles into cyclotron intended for changing physico-chemical properties by means of the surface bombardment by particles of high energies were produced.

STABILITY OF SOME CERAMIC MATERIALS TO LIQUID METALS

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The ceramic materials have various properties - high melting temperatures, also hardness, corrosion and moister stability in various environments and high conductivity. In connection with all above mentioned the purpose of work was corrosion stability study of TiB2, ZrB2, W2B5, TiC, WC in liquid aluminium and silicon. A powder of one of noticed ceramic materials crushed and mixed with aluminium or silicon in the molar ratios 1:1, grounded in quartz vessels, in which differential thermocouple were deepened. The vessels vacuumed, evacuated and placed in an isothermal zone of the electric furnace.

The mixtures with aluminium heated up to 1000 K, for silicon containing composition up to 1700 K, accordingly. At melting temperature for each metal was observed fast temperature rise, which testified interaction of liquid metals with ceramic materials accomplished by large exothermic effects.

After endurance of mixes at noticed temperature during 30 and 60 min, obtained ingots are homogeneous and had characterized by high microhardness. Monolithic ceramic materials samples were studied, using preparation technique conserved on placing them in alumna crucible with liquid aluminium or silicon. It has been appeared that samples with sizes of 5x15x30 mm dissolved completely during 30 min, forming homogeneous alloys. For such behavior explanation ceramic materials has been studied with thermodynamic method application, using own as well as well-known handbook data. It has been established, that the first stage of processes of dissolution TiB2, ZrB2, W2B5, TiC, WC in liquid metals is accompanied by allocation of a plenty of heat. The determined values of processes` thermal effects in which the alloys with mol fraction of composition of Zr, W, Ti, C equal 0,1 are formed, also for B – 0,2 in the investigated liquid metals are given below (in kJ/mol).

	TiC	TiB2	ZrB2	WC	W2B5
Al	4,9	10,8	5,7	-9,3	-7,6
Si	-6	10,2	7,2	-14,5	-5,7
Fe	9	3,3	2,7	-4,7	-17

Solutions formation (c (Zr), (W), (Ti), (C) = 0,1, and c(B) = 0,2), basically, occurs with small endothermic effects. As for direction of spontaneous process course needs ΔG values, and because of necessary data absent, we have simulated it, using ΔS for ideal solutions. It has been appeared negative ΔG magnitudes. So, the observable effects are natural also on this model possible to predict thermodynamics data both for our objects, and for similar by them (for example, for liquid iron).

CONTACT AND CAPILLARY INTERACTION Si_3N_4 OF CERAMICS WITH MELTS COPPER AND TIN

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The contact and capillary interactions of ceramic materials on a basis oxydes, nitrides and carbides of metals usually connect to power of interaction of components melts with a non-metal component of the given connections (oxygen, nitrogen, carbon). The works of last years have shown, that an essential role in these processes play and rather inactive to non-metals elements. In this case power of interaction of these elements with metal of ceramics is determining. In the given work the interaction Si_3N_4 with melts Cu and Sn in vacuum is investigated at 1423 K a method of wetting, optical and scanning microscope, profilometric of a surface of contact of melt with ceramics. Is established, that compact the siliciumnitride ceramics in Cu is dissolved with speed 2-3, and in Sn - 0,01 microns/hours.

It is confirmed by thermodynamic accounts. As at contact melt with ceramics at the first stage the indefinitely diluted solution Si in liquid metal should be formed, it can be presented by the equation:

$$Si_3N_4 + M = [Si]\,M + 2N_2.$$

Using the most authentic thermodynamic data on properties melts of binary systems Cu (Sn) - Si and $_fG$ (Si_3N_4), we have calculated G and H of this reaction. But the process of interaction can proceed further before formation of a solution with mol fraction of silicon 0,1 and more. An estimation G of processes therefore is executed, in which the solutions more enriched by silicon are formed. The results of accounts H, G kJ/mol) of reactions proceeding on border of the unit ceramics liquid metal, are given below:

Металл	H([M])	G([M])	$G(M_{0,1})$	$G(M_{0,2})$
Sn	70	23	9,6	11,8
Cu	-80	-63	-1,3-	1,2

It is clear, that the tin should not cooperate with Si3N4 even at the first stage. On the contrary, Si_3N_4 with Cu can react with formation of solutions with the maximal concentration of silicon 0,15.

So, the thermodynamic method is possible with success is to applied to forecasting features of interaction on border of the unit with ceramics liquid metal.

NEW GENERATION OF STRUCTURAL CERAMIC MATERIALS BASED ON ZrO_2

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The unique combination of high strength and fracture toughness, stability to influence of corrosive medium, low thermal conductivity and especial electrophysical properties is responsible for the promise of the application of the ZrO_2 - ceramic materials in the immediate future. Our combined approach to improvement of the ZrO_2 - ceramic materials consists in establishment of the non-separable line-up: producing of starting powders - forming of green bodies - sintering - mechanical properties of ceramic. This non-separable technological line-up allows to construct the ceramic materials (including "self-reinforced" and layered) in the systems ZrO_2-Y_2O_3, ZrO_2-CeO_2-Y_2O_3, ZrO_2-Y_2O_3-CeO_2-Al_2O_3 at the microstructural level.

The aim of this paper is to indicate the necessity of the correlation between all steps of microstructural designing of the ZrO_2-ceramic materials.

The main attention under producing of the starting nanocrystalline powders of complex composition is given to the combined method of hydrothermal synthesis and sol – gel technology. The powder activity which provide the high strength behaviour of ceramics is occurred on this step. Slip casting followed by cold isostatic pressing provide the creation of the "regular" microstructure of monolithic and layered green bodies . The sintering conditions variation allows to receive the structural materials based on ZrO2 with fine-grained, two-scale "self-reinforced", layered microstructures.

The structural materials with bending strength of 1000 – 1200 MPa and K_{1c} - up to 15 - 20 MPa.m ^{0,5} were produced as a result of this complex approach.

The following technology are developed: targets for electron-beam plotting of heat-protective coatings ; cutting ceramics for various purpose; dies for spraying of abrasive, loose and liquid materials; drags for drawing of an aluminium and copper wire; crucibles and shell forms with the covering layer for melting of refractory, chemical active metals and alloys (up to 2000^{0}C); high-temperature heaters for exploitation in an oxidising medium at the temperature up to 2000 ^{0}C in the conditions of repeated switching on / switching off.

Phase Formation during interaction of composites of the Si_3N_4-Al_2O_3-AlN-TiN system.

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This work is devoted to studying of the phase formation processes during interaction of composites of the Si_3N_4-Al_2O_3-AlN-TiN system under conditions, approximated to condition of hot molding of them, and to spontaneous compression of composites, promoting the improvement of some mechanical characteristics of sintered materials.

Using differential thermal and X-ray diffraction analyses, composites of the Si_3N_4-Al_2O_3-AlN-TiN with content of TiN, equal to 10, 25 and 50mol.%, are investigated. It was shown, that during heating of the specimens up to 1900^{0}C, i.e. at conditions of hat molding of composites, interaction of Si_3N_4 with Al_2O_3 with formation of β-sialon, mullite, X-phase and SiO_2 takes place. Beginning from 1600^{0}C, the partial dissociation of Si_3N_4 to free silicon and nitrogen, that proceeds completely at 1900^{0}C, takes place. And appearance of free silicon determines further behavior of compositions, rich in nitrides of silicon with TiN, disilicide of titanium, that takes part in eutectical reactions $L_1 \leftrightarrows Si+TiSi_2$ (1320^{0}C) and $L_2 \leftrightarrows TiSi_2+TiN$ (1208^{0}C), forms.

In the range of compositions, rich in Al_2O_3, the processes of interaction Al_2O_3 with AlN, leading to formation of spinel AlON (1700^{0}C-2050^{0}C) and eutectic of it with Al_2O_3 at 1850^{0}C, predominate. Presence of eutectical liquids promotes liquid-phase sintering of composites, that leads to spontaneous compression of materials. That's why obtained results can be used at selection of optimal conditions of creation of instrumental materials based on silicon nitride with improved characteristics.

CERAMIC COMPOSITES BASED ON Si_3N_4-TiN.

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This work is devoted to obtaining and investigating the Si_3N_4-TiN ceramic composites with sintering additives of Y_2O_3, Y_2O_3-Al_2O_3 and Al_2O_3, based on nanosized powders and produced by hot-pressing. The structure, phase composition, tribology, and physico-mechanical properties such as hardness, fracture toughness, strength and wear resistance have been studied as a function of the TiN content in the Si_3N_4-TiN composite materials.

It has been demonstrated that it is possible to get a high density material Si_3N_4-(30-50)wt.%TiN composite with good physico-mechanical properties without any additives by hot-pressing (HV-16.5GPa, K_{1c}-6.3MPa*м$^{1/2}$, strength-595MPa). Alumina is an excellent sintering additive for all Si_3N_4-TiN compositions of ceramic materials for cutting tools and gives a possibility to produce ceramic materials with improved physicomechanical properties (HV-19GPa, K_{1c}-8.0MPa*м$^{1/2}$, strength-800MPa). Y_2O_3 as sintering additive is only suitable for composites based on Si_3N_4 (TiN<50%).

Hardened steel can be turned by Si_3N_4-(25-70)wt.%TiN materials for cutting tools, but high-chromium steel is better to turn by ceramic composites based on TiN (TiN>50wt.%).

The Si_3N_4-20wt.%TiN composites demonstrate the best wear resistance in friction with abrasives, however in friction with hardened steel the best wear resistance is demonstrated by the Si_3N_4-70wt.%TiN composites. Thus, the optimal field of the Si_3N_4-TiN ceramics compositions for application has been determined.

The effect of additive content as well as TiN content in the composition of hot-pressed material on the structure and phase composition of produced ceramics has been revealed.

PHASE DIAGRAMS OF THE SYSTEMS $Al_2O_3 - ZrO_2$ – RARE EARTH AND Y OXIDES AS A BASE FOR CREATING NEW STRUCTURAL AND FUNCTIONAL CERAMIC MATERIALS

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Systems $Al_2O_3 - ZrO_2$ – rare earth and Y oxides attract attention as a source of numerous srtuctural, functional as well as refractory materials.

Interaction in binary bounding systems $Al_2O_3 - ZrO_2$, $ZrO_2 - Ln_2O_3$ and $Al_2O_3 - Ln_2O_3$ are largely studied and almost all of the phase diagrams are constructed. It helped us to forecast the interaction in the ternary sustems mentioned above. According to the results of this prognosis all systems studied were divided into 5 groups and a repesentative from every group were experimentally investigated as well as the system $Al_2O_3 - ZrO_2 - Y_2O_3$. Thus the systems including La, Nd, Sm, Er, Yb and Y oxides were studied.

Interaction in the systems was studied in the temperature range 1250 – 2500 °C by phase diagrams constructing in the form of solidus and liquidus surface projections, isothermal (at 1250 and 1650 °C), quasibinary and polythermal sections.

Specimens were produced by chemical and ceramic methods and explored with DTA, X-ray, petrography and microstructural methods.

Interaction in the systems are eutectic mainly. Ternary solid solutions and compounds were not found. The ZrO_2-phases as the most thermodynamically stable determine the systems triangulation. The primary crystallization fields of these phases occupy the largest area of liquidus surfaces. It was shown, that because of the solid solutions formation in bounding binary systems $ZrO_2 - Ln_2O_3$ the ternary systems $Al_2O_3 - ZrO_2 - Ln_2O_3$ have partially quasibinary sections only. Phase transitions in ZrO_2 and Ln_2O_3, that display themselves in binary bounding systems as metatectic points, give rise to peritectic reactions in the ternary systems.

The results obtained allow to forecast the interaction character in other ternary systems of lanthanoid series. Because of its preferentially eutectic character we can recommend these systems for creating composite ceramic materials for new industrial applications .

REGULARITIES AND FEATURES OF PLASTIC DEFORMATION AND STRENGTHENINGS OF POROUS TERNARY COMPOUND Ti_3SiC_2 AT AN UNIAXIAL COMPRESSION

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Cylindrical samples of diameter d=10 mm and height h=10 mm produced by a sintering of mixture of TiH_2-TiC-SiC powders in vacuum. The obtained phase composition correspond to stochiometric a composition Ti_3SiC_2 with the small additives TiC and $TiSi_2$. The initial porosity made θ=0,41. An uniaxial compression conducted at T=1100-1300 °C and $\varepsilon = 10^{-3}$ c^{-1} in vacuum.

Experimentally set that the lowering of a porosity of the given material starts after reaching strain at a level ε=0,1 and submits to dependence $\lambda = K_\theta \varepsilon - \lambda_o$. Here $\lambda = \Delta\theta/\theta_o$ - relative lowering of a porosity of a sample; $\varepsilon = \Delta h/h_o$ - relative decreasing of height of a sample; K_θ- coefficient of lowering of a porosity; λ_o - value of slowdown of lowering of a porosity. The obtained dependence allows to install a relation between current decreasing value of height of a sample and relevant value of its porosity at an uniaxial compression $\theta = \theta_o(1+\lambda_o - K_\theta(h_o - h)/h_o)$. In addition it is obviously possible to receive concrete value of coefficient of decreasing of initial height of a sample for production nonporous state of a material $K_h = (K_\theta - \lambda_o - 1)/K_\theta$.

The analysis of process of deformation strengthening of porous compound Ti_3SiC_2 was conducted in conditions of maintenance of homogeneity of strain of a sample on its volume (absence of "barrel"), constancy of deformable volume, and also in view of current lowering of a porosity at compression. Set that strain hardening of this porous material at a temperature level T=0,45 T_m submits to the same regularities, as compact: intensive strengthening at the first stage (in limits of values of true strain e=0,02-0,07); maintenance of the index of strain hardening at a stage of strengthening equal n=0,9; the subsequent weakening, presented by effect sequentially of flowing past processes of dynamic recovery, polygonization and recrystallization. Distinctive features of a porous material are lower values of true stresses (S), normalized to a nonporous state, higher values of strain of a beginning of a weakening and fracture strain. The representation of the compression diagrams in coordinates $S\text{-}e^{0,9}$ has allowed to install true values of the characteristics of strengthening: a coefficient of strain hardening K_1 and critical strain of a beginning of a weakening e_{cr}.

THERMAL ACTIVATION ANALYSIS OF TEMPERATURE AND TIME DEPENDENCES OF A HARDNESS OF POROUS TERNARY COMPOUND Ti_3SiC_2

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By method of measuring of hardness (P=10 H, T=20-1200 °C, t=1-60 min.) studied features and mechanisms of a plastic deformation of porous ternary compound Ti_3SiC_2. Cylindrical samples of diameter d=10 mm and height h=10 mm produced by a sintering of mixture of TiH_2-TiC-SiC powders in vacuum. The obtained phase composition correspond to stochiometric a composition Ti_3SiC_2 with the small additives TiC and $TiSi_2$. The maximum porosity made θ=0,41.

By results of measuring short-time (1 min) hardness of compound with a porosity θ=0,41 it is shown that in an interval of temperatures from 20 up to 700 °C the lowering of hardness practically misses, while at T> 800 °C – it is sharp and considerable (the value of hardness is diminished with HV=500 MPa at 700 °C up to HV=200 MPa at 1200 °C). The existence of three temperature intervals distinguishing in mechanisms of a plastic deformation sets: T=600-800 °C , U=0,10 эВ, overcoming by dislocations of an internal resistance of a crystal lattice, i. e. Peierls – Nabarro stresses; T=800-1050 °C , U=0,53 эВ, the overcoming of interaction of dislocations with impurity atoms of interstitial in a metal sublattice (it will be formed by bonds Ti-Si); T=1050-1200 °C , U=2,2 эВ, migration of vacancies in metal and carbon (Ti-C) sublattices of compound Ti_3SiC_2.

Study of long-term hardness (t=1-60 min) at a stationary value to temperature in an interval T=800-1200 °C has shown, that the process of a weakening of this material submits to dependence such as $H=at^{-n}$, starts at T> 800 °C , slowly grows at elevation of temperature up to T=1100 °C (index of a weakening increases from value n=0 up to value n=0,15) and increases sharply at overflow of this temperature (at T=1200 °C we have n=0,43). The critical quantity of time, after which reaching the intensive weakening starts in this interval of temperatures, makes 10 minutes.

Lowering of a porosity of a material up to value θ=0,19, obtained by an single-axis compression of a sample at 1300 °C , i. e. followed by deformation strengthening, has given in considerable elevation of hardness (in 2,5-3 times). Nevertheless, the character of temperature and time dependences of hardness has remained former, and the temperature intervals of development of different mechanisms of a plastic deformation and value of the thermal activation characteristics were maintained invariable.

MACROSCOPIC AND MICROSCOPIC ASPECTS OF DESIGNING POROUS CERAMIC MATERIALS

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A detailed analysis of phenomena connected with the designing of **porous ceramic materials (PCM)** obtained by sintering grain materials of respective size and shape has been carried out in this work. The effect of both macroscopic and microscopic features on the main parameters of such materials, and first of all on their open porosity, pore size and mechanical properties, have been discussed.

Macroscopic aspects of designing PCM first of all consist in: pore size and shape, amount of binder added and its spatial distribution, number and distribution of pores, pressing pressure, sintering temperature and time as well as heating and cooling rates.

Microscopic aspects of designing PCM first of all consist in:

- processes occurring on the grain-binder border, which depend on the type of grain and binder, grain and binder coefficient of expansion, softening point or binder sintering temperature, grain wettability with the binder as well as binder reactivity with respect to the crystalline grain;
- physical-chemical processes occurring both in the grain as well as in the binder, e.g. crystallization, martenzitic transformations, order-disorder transformations, e.t.c.

It was found that physical-chemical processes occurring during sintering, proceeding on the grain-binder interface, besides the type and size of grains of the grain material, its chemical and phase composition as well as the type and amount of binder, affect the properties of porous grain materials.

MICROSTRUCTURAL CHARACTERISATION OF CERAMIC VITREOUS SYSTEMS

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The current trend for prosthetic devices is the application of ceramic coatings on supports of different nature (*i.e.* mechanically more similar to bone) for an improved functional performance. The research activity reported is devoted to biocompatible ceramics coatings such as ceramic-vitreous systems to obtain surfaces capable of self-anchoring to bone tissue.

The behaviour of Yttria stabilised Zirconia (ZrO_2), either coated with a bioglass named RKKP bioglaze or uncoated, was evaluated *in vitro* and in animal models to test biocompatibility and osteointegration rate. RKKP bioglaze - coated ZrO_2 cylinders and uncoated ones as controls were implanted in the distal femoral epiphyses of 14 Sprague. To characterise the coating-substrate interface and the mechanism of adhesion, micro-analytical investigations were carried out by XRD, SEM and EDS analysis.

SECTION D. FUNCTIONAL CERAMICS: PROPERTIES; INDUSTRIAL APPLICATION **143-202**

BORON-CONTAINING PTCR $BATIO_3$-MATERIALS WITH A WIDE TEMPERATURE RANGE OF SINTERING

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PTCR materials based on barium titanate are prepared in a narrow temperature range at temperatures of *ca.* 1350^{0}C, which complicates their manufacturing technology. Introduction of sintering aids in the posistor materials, in particular, boron-containing dopants, is one of promised ways of expansion of their sintering temperature range.

The purpose of the present work was to study the effect of boron-containing dopants (B_4C, BN) on the formation of PTCR materials based on barium metatitanate ($BaTiO_3$) and its electrophysical properties.

Thermogravimetric analysis showed that in systems based on $(Ba,Y)TiO_3$ a decrease of oxidation temperatures of boron-containing compounds (10 mol.% B_4C or BN) is observed in comparison with oxidation of individual compounds – boron carbide or boron nitride. XRD showed that boron carbide oxidized at 800-950^{0}C, boron oxide formed interacts with barium titanate with formation of double barium-titanium borate, which, in accordance with results of thermogravimetric analysis, is accompanied by exothermic effect at 850^{0}C. The oxidation of boron nitride occurs in a temperature range of 900-1000^{0}C, in this case double barium-titanium borate is also formed, and exothermic effect is observed at 950^{0}C: $BaTiO_3 + B_2O_3 \xrightarrow{950^\circ C} BaTi(BO_3)_2$. The significant decrease of intensity of barium titanate XRD reflexes after heat treatment at 1300^{0}C indicates the formation of boron-containing glasses. Data of electronic diffuse reflection spectroscopy of systems investigated show that increasing the boron-containing dopant content increases the amount of $Ba_6Ti_{17}O_{40}$ phase (characteristic jogs in electronic diffuse reflection spectra at 710 nm) and Ti^{3+}-containing phase (jogs at 560 nm). $Ba_6Ti_{17}O_{40}$ is reduced at lower temperatures in comparison with $BaTiO_3$. The low-melting boron-containing phase formed at grain boundaries interferes with fast oxidation of grains on cooling, therefore the sintering temperature of PTCR materials decreases by 50-60^{0}C. Non-ferroelectric boron-containing interlayers, disposed between ferroelectric barium titanate grains, decrease the temperature dependence of resistivity in the range 200-300^{0}C, expand the temperature range of PRCR materials utilization. The investigation of microstructure of $(Ba,Y)TiO_3$-based samples with additives of boron carbide and boron nitride shows that average grain size decreases with increasing dopant amount, which causes weak varistor effect in materials.

CERAMIC COMPOSITE FILTERING ELEMENTS

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The porous ceramic materials find wide application in filtering devices. They play an important role in productions of many industries, which are connected with processing and clearing liquids and gases, for example, chemical, metallurgical, pharmaceutical, hidrolysis, machine-building and other branches.

The porous ceramic filtering materials are corrosion-resistant, wear-resistant, cheap, the stocks for their manufacture are inexhaustible.

The researchers of RIIP work at creating porous nontight ceramics materials for filtering elements. These elements are made on the basis of local mineral raw material, collateral products of ceramic manufacture. The main part of this work is closely connected with study of influence of the basic technological parameters on products properties, choice of structures, which should have the best operational and economic parameters.

The researches have shown, that using reject of manufacture of porcelain, china sanitary ware, chamotte on the basis of refractory clay are rather effective at hydrodynamical pressing the application porous ceramics materials

Study of dependences determining property (porosity, permeability, durability) ceramics received from reject of manufacture of porcelain has shown, that the sintering at temperature 1100-1150 0C provides their maximal meanings at reception of sufficient durability.

The received porous ceramics for filtering elements has enough high chemical stability, thermal resistance, that will allow to use various kinds of their regeneration: high-temperature processing, chemical influence, purge under pressure and others.

The axisymmetric products with diameter from 70 up to 120 mm and length 500 mm are characterized sufficient porosity 38-45 %, productivity on water 5-15 t/hour*m2, resource of work before regeneration up to 1200 t/m2 and can be applied for filtration of water, different liquids or air clearing.

CHARGE TRANSFER PROCESSES IN β-$Si_{1-x}Ti_xC$

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It is known, that the problem of ionic-covalence degree chemical bonding definition in the wide-band semiconductor materials is connected with the problem of impurity atoms site localization definition. We can conclude, that the crystal silicon have a covalence type of interatomic bonding, and Me3d-impurities atom locate, as a rule, in the inculcation position, but not replace site.

Silicon carbide is a promising wide–band semiconductor material possessing high heat conductivity, mechanical strength, thermal- and radiation-stability. Introduction of 3*d*–metals into a silicon carbide substrate during synthesis or additional treatment makes it possible to vary the properties of the obtained materials substantially.

Earlier interatomic interactions in Si–(Me3*d*)–C systems were previously studied both by experimental and theoretical techniques. From references is known, that .in Si_3N_4–TiC reaction products contain mainly SiC and Ti(C,N) phases. It was found by the model pseudopotential method that for the SiC(001)/Ti interface Ti–C bonds are characterized by strong covalent C2*p*– and Ti3*d*–AO interactions. In the case of Si interface Si–Ti bonds are of a metallic character.

In this work the presence of a charge titanium atom impurity in an interstitial Si–T_d site was simulated by the $[Si_3Ti(i)C_{10}]^{24-}$ cluster. The X_α discrete variation (X_α–DV) method was used as the main method for calculating the electronic structure parameters. The computations were performed in the context of the electronic density functional theory by the self-consistent spin–unrestriction method.

The coordination polyhedron of a titanium atom in the considered position is formed by three silicon atoms and one silicon vacancy, which are the centers of carbon tetrahedrons. The break of local T_d symmetry environment of impurity atom results in origin local magnetic moment 1,33 μ_B on the impurity atom Ti. By the results of calculations impurity Ti atom in Si_4-T_d i-position interactions both silicon atoms and carbon atoms, composed the environment of Si-vacancy. In the first the Ti3d-Si-AO investigation have a basic character. And in the second Ti-C bonding have the nature of charge C->Ti transfer, and this is the origin of beginning vacancy states in Ci2p- and Ti3d-bands.

CERAMIC FILMFORMING MATERIALS FOR OPTICS: STATUS AND PROSPECTS

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The general status is considered in the field of development of ceramic materials intended for drawing of the optical coatings or filmforming materials (FFM).

Table

General characteristics of filmforming optical materials

Type of FFM (examples)	Optical range of application	Refractive index	General characteristics
Oxide (SiO_2, TiO_2, ZrO_2)	Near UV, visible, near and middle IR	1,5÷2,5	High durability, transparency, insufficient stability
Fluoride (CaF_2, Na_3AlF_6, PbF_2)	Far and near UV, visible, near and middle IR	1,3÷1,8	Insufficient durability and stability, high transparency
Chalcogenide (sulfide, selenide, telluride) Sb_2S_3, ZnS, ZnSe, PbTe)	Visible, near – far IR	1,8÷6,0	Low durability, frequently toxicity, insufficient stability

As follows from the table used now FFM do not correspond to all requirements concerning optical and operational parameters.

On the basis of the concept of the stabilisation of valence state and structure the approach to essential improvement of traditional materials and creation of essentially new materials is developed. FFM of new generation on the basis of complex compounds and compositions allow to receive optical coatings with the required characteristics.

ESTIMATION OF QUALITY PIEZOCERAMIC FOR POWER ULTRASOUND

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The comparative analysis domestic piezoceramic with import is carried out. It is shown that alongside with the complex parameters describing piezoquality $Kp^2 \cdot Qm$,, intensity of radiation $(d_{31} \times V_{зв})^2 \cdot 1\tilde{0}^{14}$, eff radiators $Kp^2 tg\delta$, for the coordination of generators with piezoconverter the important role is played with temperature stability of capacity and resonant frequency.

Researches piezoceramics from lines new piezoceramic materials PZT-system on a breadboard model of a hydroacoustic radiator are carried out.

Influence of materials of electrodes on electrophysical parameters piezoceramic elements is investigated.

Influence of effort pressure piezoelements in metal equipment on radiating properties of the converter (intensity of radiation, frequency of resonant fluctuations etc.) Is investigated and the revealed dependences are discussed.

The received results testify to conformity developed piezoceramic to the best foreign analogues, that proves to be true its use in industrial (ultrasonic baths) and household (sprays of a fuel mix in engines of internal combustion) ultrasonic installations.

HYDRATION-DEHYDRATION PROCESS FOR OBTAIN A HEAT-RESISTANT GAS CONCRETE

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Decreasing of a composite materials power-consumption is thought to be the perspective way for their development. It can be reached by decreasing the temperature of their treatment by special modes of the direct structure formation in the inorganic binders based composite materials. These materials are called 'chemically bonded ceramics' (CBCs) which refers to the both extra properties which are similar to an ordinary ceramics and ionic and covalent bonding which dominate in these materials [1]. CBCs can be obtained by usage of the environment friendly alkaline aluminosilicate binder (AAB) [2]. AAB's phase composition is presented by analogs of inorganic polymeric aluminosilicate minerals such as zeolites (after hydration), feldspathoids and feldspars (after dehydration) which characterized by domination of the covalent bonding in aluminosilicate framework [3]. AAB's obtaining principles are based on the direct synthesis of a specific phases which determinate the special properties of a material – high strength, adhesion, corrosion and heat resistance etc.

The heat-resistant gas concrete based on AAB and fly ash had unit weight of 400 to 600 kg/cub.m, compressive strength of 2 to 5 MPa and heat resistance up to 1000°C [4]. These properties are conditioned by the hydrothermal synthesis of analcime-type zeolitic-like phases which can be converted into the anhydrous ones (such as nepheline and albite) by smooth dehydration and re-crystallization without damages of the framework under the warming-up to the working temperature.

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ON DISAGREEMENT BETWEEN LOSS-ANGLE TANGENTS FOR PIEZOELECTRIC CERAMICS IN STRONG ELECTRIC FIELDS AT POWER-LINE FREQUENCIES

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It has been shown that determination of loss-angle tangent, $tg\delta_c$, for piezoelectric ceramics and related materials in the strong electric field $E \geq$ 100V/mm at a power-line frequency of 50Hz (f_1) and 60Hz (f_2) rezults in dissimilar data.

For the single-type piezoelectric ceramics, produced in the countries with different power-line frequencies accepted, the values of $tg\delta_c$ determined using Schering bridge (parallel equivalent circuit) at 50 Hz, when comparing with those determined using similar devices at 60Hz, should be divided by the factor numerically equal to the frequency ratio $K=f_1/f_2=1.2$.

In comparing $tg\delta_c$ determined at a frequency of 60Hz with that for 50Hz, the former should be multiplied by K=1.2.

The reverse is true for comparison of $tg\delta_c$ detemined at the above power-line frequencies using the bridges with a series equivalent circuit.

STRUCTURE AND PROPERTIES OF CONDUCTING TiB_2-AlN-BASED CERAMICS

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In this work, synthesis of conducting TiB_2-AlN-based system with solid green reagents has been investigated in filtration combustion mode at elevated nitrogen pressure (from 20 to 300 MPa). Effect of pressure on combustion rate and content of free aluminum in end products was studied. The green mixture composition dependence of combustion rate was determined. Composition of the end product, as well as porosity, volume resistivity and bending strength of synthesized products were examined by XRD and chemical analysis. Structural peculiarities of the SHS-synthesized system and critical concentration of titanium diboride (19% vol.) in the composition, resulted in discontinuous change in material properties, allow to suggest that the change of conducting properties can be explained by generated fractal structures.

HIGH TEMPERATURE Si_3N_4–BN COMPOSITE MATERIALS OF VARIABLE COMPOSITION

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Composite materials developed by means of hot pressing and reaction sintering processes are being considered. Silicon nitride and boron nitride were used as starting components.

The distinguishing feature of the produced composites is the possibility of properties control over a wide range by varying of ratio of starting components and thus of significant extending the range of ceramic materials application.

The unique reaction sintering technology with producing of protective layer providing the substantial increase of high temperature characteristics has been developed. Hot pressing technology makes it possible to manufacture multilayer structures with variable properties.

Thermal and mechanical properties of Si_3N_4-BN composites have been estimated. The results of testing of the articles for various applications are presented.

BORON NITRIDE FOR HIGH TEMPERATURE CERAMIC DIELECTRICS

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Traditional methods for manufacturing boron nitride (BN) such as hot pressing and pyrolytic deposition do not satisfy the requirements of modern facilities. New approaches are needed for the production of BN ceramics. Lately a series of BN materials has been developed, which has advantages in comparison with pyrolytic and hot pressed BN, not only in the level of achieved properties, but in workability too. These materials were obtained by casting in steel moulds or hydrodynamic machines and post sintering. In this way, reaction sintered ceramics from turbostratic powders with additions of amorphous boron is obtained. The material is distinguished by high purity (BN – 99,5 wt.%, B_2O_3 – the main impurity), stable values of strength and dielectric characteristics at temperatures to 2273K. The material is isotropical and has excellent thermal shock resistance. Using reaction sintered BN ceramics as porous, chemically inert matrix for processing it by the element organic compounds, we succeeded in obtaining isotropic material with the strength level equal to the strength of pyrolytic BN at temperature 1773K. The material is transparent in the microwave range up to 2273K. Production procedures for sintered BN chemically toughened by impregnation with organosilicon compounds, BN-AlN-Al_2O_3, BN-AlN-AlB_x, BN-SiAlON composites and materials obtained by thermal molecular linkage are described.

ADHESIVE COMPOSITION IN SiO_2–Al_2O_3–P_2O_5–B_2O_3 SYSTEM

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High-temperature ceramic adhesive based on phosphate binders has been developed at TECHNOLOGIYA (Obninsk, Russian Federation). It is intended to cement together and reclaim articles made of technical ceramics:

* screens of electrically heated furnaces;
* lining of tunnel-type furnace cars;
* ceramic articles employed in the process of glass bending;
* ceramic engine components;
* thermocouple protective sheathes.

This is applicable to mullite, mullite-corundum, corundum refractories, silicon nitride and silicon carbide ceramics.

The adhesive is stored and delivered in the form of isolated components, the mixing is done just before application. The adhesive line thickness can be chosen at will.

The adhesive is also available in a ready-made form in an air-tight package and it retains its properties during 30 days. In the air the adhesive is viable not less than 30 minutes.

Technical characteristics:	
Operating temperature	– from 60 to 1650°C;
Adhesive line thickness	– 0.1 – 3.0 mm;
Adhesive line shearing strength (depending on material and its porosity)	– 5-20 MPa.

Structural arrangement of hydroxyl and phosphate groups plays an important part in the formation of the adhesive composition in SiO_2–Al_2O_3–P_2O_5–B_2O_3 system. During thermal treatment free (100-150°C) and crystal – hydrate (250-400°C) water is released, PO_4 groups fit into the structure of mullite sillimanite strips and the carcass of phosphocrystobalite structure is initiated.

Then secondary mullite and berlinite are formed whereupon the latter is recrystallized into phosphocrystobalite (800-900°C). The structure of mentioned phases is straightened out at 1000°C. At the same time the process of glass formation takes place. First alumoborophosphate glass is formed and then silicophospate (1000-1200°C) and zirconia (1550°C) glasses are formed.

OBTAINING CERAMIC BORIDE`S OF COVERS IN REQUIREMENTS THE SELF-PROPAGATION`S OF HYGHTEMPERATURE SYNTHESIZING

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SHS - the process - new know-how of obtaining of ceramic materials and covers, founded on direct synthesizing of high-melting inorganic connections and intermetallic compounds in heat generating reactions between chemical members [1].

In activity the deposition of complex covers was investigated on the basis of borons in combustion regimes SHS - systems on steels of mass assigning. The initial contents of components ceramic SHS - mixes determines a thermal picture of process. It is ground of the thermal and thermodynamic analysis of reactions SHS - systems it is possible to speak about four kinds of chemical transmutations which are flowing past in considered systems: reaction of thermal spontaneous combustion, decomposition reaction of the carrier, chemical transport reactions, exchange reaction with a substrate.

On the basis of experimental data the nomographs linking initial powder structures with maximum temperature of process in a mode of thermal spontaneous combustion are obtained. Diluting base mix by inert matters down to 80-85 % of weights. It is possible to achieve a decrease of maximum temperatures of process up to technologically indispensable.

Borating`s the layer obtained in requirements of thermal spontaneous combustion SHS - of systems, can be both single-phase, and two-phase, consisting from (Fe, Cr, Al) B and (Fe, Cr, Al) 2 B. The doped maximum boride places in a surface zone and has a needle-like constitution. With increase of time of isothermal endurance quantity of a phase (Fe, Cr, Al) B is augmented.

The microhardness highboride`s of a phase oscillates from 18000 MPa up to 20000 MPa, and phase (Fe, Cr, Al) 2 B - from 13500 MPa up to 15000 MPa. Is established, that the time of isothermal endurance does not influence hardness of doped phases of borides practically.

In activity the regularities of formation multicomponent boride`s of covers are established, the operating characteristics of steels with multicomponent boride`s by covers are established. Is rotund, that on the parameters the ceramic multicomponent covers on the basis of borons surpass singl-component in 1,5 - 7 times.

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PRODUCTION AND MEMBRANE PROPERTIES OF POROUS MATERIALS OF SIALONS AND SILICON CARBIDE

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The microporous materials from sialons and silicon carbide are produced by reaction sintering at negative volumetric effects. The reactions, utilised, tab.1: 1- synthesises sialon by kaolin carbonitridation; 2 - silicon carbide synthesis by silicon oxide carbothermal reduction; 3 - SiC synthesis of elements.

The table 1

Carbon content both magnitudes of mass and volumetric effects

Reaction	C, masses. %	Δm, %	ΔV, %
1. Carbonitridation of kaolin	20	-40	-45
2. $Si + C \rightarrow SiC$	30	0	-29,8
3. $SiO2 + 3C \rightarrow SiC + 2CO$	37,5	-58,3	-71,2

Produced sialon stuffs have a porosity 50-60 %, silicon carbide 2 - 50 %, 3 - 85 %. The pore size of all stuffs varieties is about 1 micron and their heightened gastightness - 0,02-0,04 мкм2. To determine the selectivity of the synthesized membrane stuffs the tests on model solutions containing admixtures, most representative for industrial waste and natural waters, table 2, were conducted.

The table 2

Tests results of sialons and silicon carbide membranes

Stuff and pore size, micron		an admixture both initial densities (мг/l) and chromaticity (o) of solutions			Purification*	
					1	2
SiC	1,0-1,2	Phenolum	50	-	55	-
sialon	0,8-1,0	Zinci sulfas of cuprum (II)	50	-	82	-
sialon	0,7-1,0	Ferric chloride	50	150	60	75
sialon	1,1-1,2	humic connections	-	200	-	85
sialon	0,7-1,0	Ferric humates	120	300	70	80
sialon	1,1-1,2	Ferric humates	25	80	75	80

* Efficiency of purification, %: 1- by density, 2 - by chromaticity

The materials ensure a degree of purification from Phenolums, ions of cuprum (II), Ferri (III) on 60-85 of % at initial density of 25-50 мг/l, considerably reduce chromaticity and muddiness of water.

INFLUENCING OF FOAM CERAMICAL FILTER ON COMPONENTS DISTRIBUTION IN SILUMIN

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Foam Ceramical filters (FCF) are usually applied to lower defects of casts on nonmetallics. The real effects FCF on alloys is much more strongly and frequently the cause of failures at using FCF . The FCF influence on components distribution in complex alloy B124, concerning to an aluminum - silicon-copper-magnesium system is studied. A glass grid with the technical specifications 6-11-318-78 and FCF of cordierit porcelain with an average cell diameter from 2 up to 3,5 mm were used as filter materials.

The casts were manufactured on a foundry of expermental –industrial production of joint-stock company of "AUTOVAZ".

The quantitative performances of changes in elements distribution between aluminium solid solution and intermetallic compounds structure are obtained by means of X-ray diffraction and microX-ray spectral analyses (see tab.)

The datas are given for alloy after heat treatment. A ratio of aluminum and silicon in alloy was determined by a ratio of two neighboring spikes intensities Al (220) with $d=1,43_{30}$ (I_{Al}) and Si (311) with $d=1,63_{63}$ (I_{Si}). The less I_{Al}/ I_{Si} the more free, not dissolved in aluminium solid solution and not included in the of intermetallic compound structure of silicon contains alloy.

Conditions of a filtration	without the filter	a screen filter	FCF
I_{Al}/ I_{Si}	0,4	2,5	1,8
The contents of cuprum, %	**1,8**/(3,6-6,6)	**1,8** /(3,6-4,2)	**2,4** / -
The contents of silicon , %	**0,6**/ 32,2; 81,1	**0,6**/ 18,9; 33,1	**0,6**/ 26,8; 63,8
The contents of Ferrouse, %	**0**/(1,3-24,4)	**0** /(1,9-7,5)	**0** /(1,9-10)

The notices: - greasy font is indicated the contents of a member in a groundmass (iron detects in alloy as a polluting admixture); - in brackets after feature - minimum and maximum contents of a member in intermetallic compounds; - after feature without brackets - mean and maximum contents of silicon in actuations.

Thus, usage of filters changes conditions of a crystallization of phases and results in change of a phase structure complex of alloy arrested even after heat treatment.

EFFECT OF THE SMALL Cr_2O_3 ADDITIVES ON THE Y-TZP PROPERTIES

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Low concentrations, up to 0.7 mole %, of Cr_2O_3 were introduced to the Y_2O_3-ZrO_2 solid solution by the physical mixing of the constituent powders or by the coprecipitation technique. It was found that the preparation method influences greatly properties of the resultant material. In the case of the coprecipitation method a solid solution in the Cr_2O_3-Y_2O_3-ZrO_2 system was formed. It was corroborated by the changes of the unit cell volume. Simultaneously, grain boundary segregation of Cr and Y occurred. In this case mainly intergranular crack propagation was observed, contrary to the physically mixed systems. The latter ones as well as "pure" Y-TZP show mixed thransgranular and intergranular fracture characteristics. Under the applied sintering conditions no symptoms of the solid solution formation were observed.

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STRUCTURAL AND SUPERCONDUCTING PROPERTIES OF THE SOLID SOLUTIONS IN THE $R_{1+x}Ba_{2-x}Cu_3O_{6,5+x/2+\delta}$ (R=Sm, Eu) SYSTEM

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The $R_{1+x}Ba_{2-x}Cu_3O_{6,5+x/2+\delta}$ solid solution (R=La, Nd, Sm, Eu and Gd) superconducting phases are promising materials for the practical applications.

The samples of $R_{1+x}Ba_{2-x}Cu_3O_{6,5+x/2+\delta}$ solid solutions were prepared by sol-gel method using ammonium citrate as gel-forming agent. The conditions for citrate gel pyrolysis were studied by IR-spectroscopy, XRD analysis and DTA/TGA. It was found that $R_{1+x}Ba_{2-x}Cu_3O_{6,5+x/2+\delta}$ phase formation from citrate precursor began at 700°C resulting from the reaction between CuO, R_2CuO_4 and $BaCO_3$. Single phase $R_{1+x}Ba_{2-x}Cu_3O_{6,5+x/2+\delta}$ phase can be obtained at 800°C.

Crystal lattice parameters behavior, oxygen stoichiometry and phase transitions in the $R_{1+x}Ba_{2-x}Cu_3O_{6,5+x/2+\delta}$ solid solutions were studied as functions of temperature and heterovalent R^{3+}substitution for Ba^{2+} parameter x. Increase of parameter x is accompanied by the increase of indifference of the structure to temperature as well as stability of oxygen sublattice. According to the results of iodometric titration the mobile oxygen content (δ) in the $Sm_{1+x}Ba_{2-x}Cu_3O_{6.5+x/2+\delta}$ solid solutions changes with x nonmonotonically while there is almost no change of δ with x for $Eu_{1+x}Ba_{2-x}Cu_3O_{6.5+x/2+\delta}$ system. Besides, dependence of crystal lattice parameters on oxygen content was established for some representatives of $R_{1+x}Ba_{2-x}Cu_3O_{6,5+x/2+\delta}$ solid solutions.

According to the results of resistivity measurements superconducting transition was observed only for the compositions with $0 \le x \le 0.1$. Critical temperatures of the cations stoichiometric compounds $SmBa_2Cu_3O_{6,5+\delta}$ and $EuBa_2Cu_3O_{6,5+\delta}$ were found to be 95 K. All other samples with $x>0,1$ have semiconducting behavior in the temperature range of 77-300 K.

SUPERCONDUCTING PHASES OF $Bi_2Sr_2Ca_{1-x}(Ce, Zr, Hf)_xCu_2O_y$ COMPOSITION

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It is known that introduction of impurity ions affects the properties of the HTSC ceramics whose composition is Bi-2212. The properties of homologous phases in the Bi–Sr–Ca–Cu–O system are changed most essentially at changing the Ca/Sr ratio. The Zr^{4+}, Hf^{4+} and Ce^{4+} ionic radii well agree with that of 8-coordinated calcium in Bi-2212. That is why it is of importance to study the effect of calcium replacement with cerium, zirconium or hafnium in the Bi-2212 ceramic composition on superconducting properties of the phases obtained. To do this, we synthesized polycrystalline superconducting samples whose composition was $Bi_2Sr_2Ca_{1-x}Me_xCu_2O_y$ (Me – Zr, Hf, Ce; $0 \le x \le 0.6$). The phase composition and crystal lattice parameters were determined for powders using x-ray diffraction (diffractometer ДРОН-3М, $Cu_{K\alpha}$-line with Ni filter). The temperature dependence of resistance was measured in the 4.2–300 K range using traditional four-contact technique.

For $Bi_2Sr_2Ca_{1-x}Me_xCu_2O_y$ the homogeneity region was shown to occur at $0 \le x \le 0.1$ when Me = Ce, Zr and only at $x = 0.05$ when Me = Hf. At higher x values the impurity 2201 phase was observed in the samples along with Bi-2212 phase, and superconducting properties got worse.

When calcium in the Bi-2212 composition was replaced with cerium, zirconium or hafnium, then the amount of superconducting phase decreased. In this case the superconducting transition temperature dropped, correspondingly, to 83 and 79.2 K (cerium content $x = 0.05$ and 0.1), 80 and 78 K (zirconium content $x = 0.05$ and 0.1) and 77 K (hafnium content $x = 0.05$).

It seems that when cerium, zirconium or hafnium atoms are introduced into the crystal lattice of superconducting Bi-2212, they change the normal ion positions in the lattice that are characteristic of the given superconducting phase. This results in localization of more electrons, thus suppressing superconductivity in the system.

INFLUENCE Al_2O_3, Nb_2O_5, ZrO_2 AND Ta_2O_5 ADDITION ON PROPERTIES SUPERCONDUCTIVE METALLOOXIDES

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The problem of corrosive stability is necessary to decide for practical utilization the superconductors. The leading of second phase can promote improving physico-chemical, mechanical and physical properties superconductive materials. Therefore the problem of searching the addition, which does not make worse the properties of superconductive materials, is very actual. (Therefore the searching of addition, which does not make worse the properties of superconductive materials, is issue of the day.)

The properties of composite materials based on superconductive ceramics $Bi_2Sr_2CaCu_2O_y$ and $Pb_{0.71}Cu_{0.29}Sr_2Y_{0.73}Ca_{0.27}Cu_2O_y$ with oxides of aluminium, niobium, zirconium and tantalum addition has been studied for this purpose.

Series of samples $Bi_2Sr_2CaCu_2O_y$+xA and $Pb_{0.71}Cu_{0.29}Sr_2Y_{0.73}Ca_{0.27}Cu_2O_y$+xA, where x = 5, 10, 15, 20 mass %, A = Al_2O_3, Nb_2O_5, ZrO_2 and Ta_2O_5 has been synthesized by (прекурсор) method. The phase composition of synthesized samples has been analyzed. The phases, which create the composite system has been identified. The dependence of quantity of superconductive phase from character and quantity doping has been found. It has been shown that increasing of quantity the doping oxides lead to decreasing the quantity of 2212 phase and to increasing the quantity of 2201 phase ($Bi_2Sr_2CuO_y$), in case bismuth ceramics. The quantity of 1212 phase is decreasing and the quantity of (гексагональной) phase $Sr_{5-x}Pb_{3+x}Cu_yO_{12-\delta}$ is increasing, in case of $Pb_{0.71}Cu_{0.29}Sr_2Y_{0.73}Ca_{0.27}Cu_2O_y$ ceramics.

The dependence of crystalline parameters from ionic radius of metal, which is including the doping, has been found.

The influence of oxides of aluminium, niobium, zirconium and tantalum on superconductive properties of synthesized ceramics has been analyzed. It has been determined that the critical temperature of composite samples slightly low then the critical temperature andopinng $Bi_2Sr_2CaCu_2O_y$ and $Pb_{0.71}Cu_{0.29}Sr_2Y_{0.73}Ca_{0.27}Cu_2O_y$ samples. The worsening of superconductive properties can be concerned with extension unsoundness of the structure. The correlation between onset critical temperature and ionic radius of metal, which is including the doping oxide has been made.

The influence of doping on degradation poses of Bi-2212 and Pb-1212 phases under water, steam and carbonic gas has been studied. It has been achieved that overstoichiometric addition of oxides Al_2O_3, Nb_2O_5, ZrO_2 and Ta_2O_5 is augmenting the stability of superconductive ceramics. The optimal composition of doping, which make speed of degradation HTS phase a minimum, has been found.

TECHNOLOGY, HETEROGENEITY AND PROPERTIES OF MANGANITE-LANTHANUM CERAMICS WITH A COLOSSAL MAGNETORESISTANCE

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Manganite-lanthanum ceramics, owing to a colossal magnetoresistive effect (CMRE), is among the most interesting and prospective materials [1] for production of engineering. The CMRE values of this multifunctional ceramics is the order of magnitude higher than that of metallic thin-film ones used in electronics.

The application of these new materials is restrained by the absence of physico-chemical and technological grounds and by debates on the nature of the colossal magnetoresistive effect. To meet the lack, the X-ray diffraction, magnetic, resistive and NMR investigations have been performed of the influence of composition and technological parameters (T, P) on structure and properties of ceramic samples of some most prospective manganite-lanthanum systems of the perovskite structure. They are self-doped $La_{1-x}Mn_{1+x}O_{3\pm\delta}$ [2] and alloyed solid solutions $La^{3+}_{1-y}Me^{2+}_{y}$ $Mn^{3+}_{1-y}Mn^{4+}_{y}O^{2-}_{3\pm\delta}$ (Me^{2+} – Ca^{2+}, Sr^{2+}, Ba^{2+}, Pb^{2+}). Compositions with x=y=0,3 are optimal. The minimal synthesis and sintering temperatures have Ca- and Sr-containing manganite-lanthanum ceramics and the maximal ones – the Ba-containing manganite-lanthanum ceramics.

The revealed correlation between the tolerance factor and the width of ^{55}Mn MNR spectrum is explained by distortions of polyhedra not only because of the difference in the radii of substitutional ions, but non-equivalent environment because of defective structure. We were the first to show that the most qualitative (of the maximal MRE and phase-transition temperatures) are compositions with an excessive superstoichiometric manganese. Such nonstoichiometric solid solutions are typical of the maximal presence of defects and structure-and-chemical heterogeneity appearing not only in the form of point defects (the cation and anion vacancies), but a more complex in-plane ones of the cluster type. Crystallochemical and magnetic nature of the clusters and their influence on resistance and magnetoresistive effect have been determined.

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MAGNETORESISTIVE EFFECT IN $La_{0.7}Mn_{1.3}O_3$ CERAMICS UNDER HIGH HYDROSTATIC PRESSURE UP TO 2,2 GPA

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The interest to rare-earth manganite ceramics is caused by a colossal magnetoresistive effect. The nature of unusual relations between electrical and magnetic properties remains debatable.

Integrated examination of resistance and magnetoresistive effect by the influence of high hydrostatic pressure (HHP) relates to the urgent scientific and engineering problem. The temperature of "metal-semiconductor" transition with HHP increase grows noticeably. In the ceramics, two phase transitions have been revealed. The main transition is in the range of maximum resistance temperature T_{ms}=235 K (H=0, P=0) and T_{ms}=275 K (H=8 kOe, P=1,8 GPa). Two peaks of the resistance are caused by mesoscopic heterogeneity of cluster type.

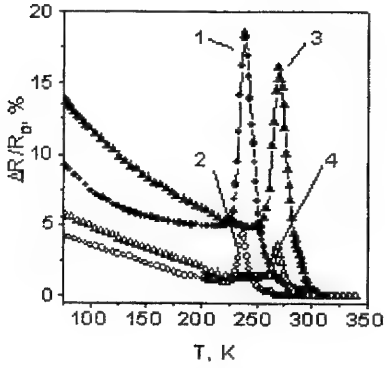

Fig. 1. Influence of hydrostatic pressure and magnetic field to MRE: *1*–P=0,H=8 kOe, *2*–P=0,H=2 kOe, *3*–P=2.2 GPa H=8 kOe *4*–P=2.2 GPa H=2 kOe.

For the ceramic sample of $La_{0.7}Mn_{1.3}O_3$ following data were obtained (fig.1): with the grow of magnetic field strength from 2 to 8 kOe the magnitude of MRE increases from 4 to 18,5 %, i.e. is 4,6 times as high. In consequence of P=2,2 GPa application at H=8 kOe, the magnitude of MRE becomes 1,75 times as less as the initial value at the same magnetic-field strength. Temperatures T_{ms} and of MRE peak – T_p vary practically linearly with the increasing of pressure that evidences the elastic range of sample deformation. The reason of such behavior may be the decreasing of interionic distances and modification of exchange interactions that shift the metal transition temperature of the sample to a higher range.

THE NANOCRYSTALLINE FERROELECTRICS: POSSIBILITIES, PROGRESS, PERSPECTIVES

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Size effect is the defining factor in the development of electronic ceramics based on ferroelectrics and barium titanate, in particular. Prospects of application the nanocrystalline ferroelectric ceramics are based on new effects inherent to this class of materials due to changing of particle size of powders or ceramic grains. The basic properties are phase transitions and dielectric characteristics, which depend on grain size. The reduction of grain size less than 1 μm is causing the changes in ferroelectrics domain structure, reducing, in turn, the dielectric constant, and resulting in changing the phase transition temperatures, that superimpose a restriction on the following miniaturization of ceramic products. To making a nanocrystalline ceramics on the base of barium titanate, it is necessary to use up-to-date methods of syntheses and sintering, which take into account the competition of thermally activated mechanisms inherent to both syntheses and sintering. This paper presents results of non-isothermal rate-controlled synthesis and sintering of barium titanate, as well as size effect revealed in nanocrystalline barium titanate. It is shown that rate-controlled synthesis from thermally unstable precursors allows us to get powder with the particle size near 10 nm. The rate-controlled sintering gives a nano-grained fully dense ceramics with the grain size substantially less than 100 nm keeping the factor of grain growing of 4÷5, which 2÷3 times less, than in traditional sintering modes. The Curie-Weiss behavior near ferro-paraelectric transition is studied depending on grain size. The prospects of using these results in multiplayer capacitor technologies are discussed.

DIELECTRIC PROPERTIES OF CERAMIC COMPOSITE MATERIALS

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Ceramic composite materials exhibit interesting combination of unusual electrophysical and mechanical properties with a high chemical and thermal stability. This makes possible to apply them in computer engineering, radio engineering and other electronic technologies.

Construction of ceramic composite materials with required (precisely defined) properties is a complex, multiparameter problem. This problem can be solved only by means of calculation techniques that can efficiently include into consideration many different variants of ceramic composite structures with the pre-required properties.

Our method of calculation of dielectric properties for ceramic materials is based on iterative averaging and renormalization group approach using a "blob" model of fractal structure [1-6]. For metal-dielectric composites we calculated critical indices of the correlation length, density of the percolating cluster, and fractal dimensionality, which are in good agreement with results of other authors. Using the concept of the Voronoy cell for the description of influence of an interphase layer on effective dielectric properties of composites, we calculated the dielectric properties in full range of concentrations of non-homogeneous material, at different frequency of external electric field. Comparison of calculated results for conductivity and dielectric permittivity showed a good agreement with experimental data.

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THE FORMATTING OF TRANSPARENT BERYLLIUM CERAMICS AND THE PERSPECTIVES OF IT APPLYING

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Today interest in transparent beryllium-oxide ceramics is the result of requirements of new technical brunches and special device-building. There is the necessity in obtaining and applying of dense transparent ceramics, possessing phys.-chemical properties similar monocrystal ones. Ceramics on beryllium oxide base is characterized with the set of unordinary properties, which provide it work as effective scintillates, working stuff in thermoluminescent, exoemission and electron paramagnetic resonance dosimeters. Today the base characteristics and electronic structure of "pure" BeO monocrystals only have been researched most completely. Practically may be used only beryllium ceramics with densities near theoretical, because light-transparent samples, used in techniques, have various shapes and sizes. The investigation of doped BeO electronic structure and it influation on phys.-chemical properties, radiate destruction processes, impurities formation, luminescent and optical characteristics of ceramics are really actual problem.

The samples of transparent BeO-ceramics have been obtained by high-temperature pressure method under next conditions: T was lower than 1520 K, pressure was about 30 MPa. Pressure was being applied in vacuum during 15-20 minute time range. Li_2O_3 was used as a doping stuff (0.4-3.0 weight %). A little quantity of boron oxide (0.01-.2 weight %) apart from lithium oxide was added in some samples. The adding of boron oxide render positive action on microstructure and optical characteristics of transparent BeO-ceramics. The density of pressed examples varied within 3.01-3.02 g/cm^3. Obtained samples are characterized with high sensitivity to ionizing radiation and wide specter range transparency. So, obtained transparent BeO-ceramics are very interesting object for using in ionizing radiation dosimetry.

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PRODUCTION of FUNCTIONAL CERAMICS FROM ZIRCONIUM CONTAINING RAW MATERIALS

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Economic issues of the development and production of new ceramic materials have recently come to dominate the field, outshining even the technological ones. Industrial production of ceramics usually involves the use of expensive chemically pure ingredients including stabilizers. The most prospective method of considerably decreasing the production cost of ceramics involves the use of multicomponent mineral raw materials, with compositions containing materials close in their properties to those that are usually used as stabilizers.

This research focused on the use of zirconium containing concentrate – baddeleite (ZrO_2 ~ 96 %) and a combined stabilizing additive based on natural magnesium hydroxide (MgO ~ 69 %, CaO ~ 11 %), which allows for the reduction of temperature of the forming of zirkonium cubic dioxide and increase the temperature of the start of eutectic disintegration of solid solutions of zirconium dioxide – magnesium oxide. Polymorphic transformations of zirconium dioxide in the temperature interval from 1000 to 1700 C. were studied during this research. We obtained high-temperature (cubic) stabilized zirconium dioxide. Physics-mechanical properties of a ceramic material produced using slicker casting technology were also studied. The produced material was used for the moulding of a ceramic crucible for the casting of dental metal.

THE THERMAL STABILITY OF STRUCTURE OF THE DIRECTLY - CRYSTALLIZED COMPOSITION MATERIALS LaB_6-$Me^{IV}B_2$.

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The eutectic alloys of systems LaB_6-MeB_2 obtained by a directional crystallization represent of natural composites, at which the matrix from lanthanum hexaboride is hardened by discrete fibers (diameter 0,3-1,2 microns and length 200-500 microns) of diboride phase. It has allowed to increase durability absolute friable LaB_6 from 80 up to 1400 MPa. As the eutectic alloys have good thermodynamic and thermomechanic compatibility with cathodes from lanthanum hexaboride, they can effectively be applied as constructional elements of cathodic - heater assemblies working in contact with lanthanum hexaboride long-lived time at operating temperatures of cathodes 1400-2000 °C. In work the temperature effect, process time, type of diboride, the initial geometrical sizes of composites structural component on the quantitative characteristics of a microstructure of the directly - crystallized alloys during high-temperature annealing is investigated.

It is shown, that the coarsening of structure of natural directly armatured composites goes on the Ostvald mechanism, by increasing of a diameter of one rods inclusions for score of diminution others. Thus the density of inclusions in a unit volume is diminished, and the effective diameter is incremented in accordance with rise of temperature and time of annealing.

It is fixed, that temperature of a beginning of intensive coarsening of structure lowest (2373 K) for composites with rod inclusions of titanium diboride, that is stipulated most by high level of thermoelastic strengths incipient near to a demarcation of phases. In accordance with diminution of a difference in coefficients of thermal expansion of matrix and diboride phases, temperature of intensive coarsening of structure increases and for LaB_6-HfB_2 makes 2473 K.

From composites the constructional elements of electron-optical systems of ionic radiants were made. After long-lived operation (500 h) at temperatures 1500-2100 K practically is shown, that the natural composites can effectively be used as high-temperature structural materials because change of structure during long-lived annealing and multiple heating - refrigeration of alloys LaB_6-TiB_2, LaB_6-ZrB_2, LaB_6-HfB_2 at temperatures smaller 2100 K practically is not observed.

CERAMIC CATHODE ASSEMBLIES FOR ELECTRON-BEAM DEVICES.

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In work the results of investigation-industrial approbation, technical and economic effectiveness and introduction of the new including boron zone melted materials at manufacture of cathodes and ceramic cathode assemblies of electron-beam devices of a new engineering are considered.

There are considered the fundamentals of technological processes of deriving of one-piece compounds between monocrystalline lanthanum hexaboride, graphite and euthectic directly - crystallized alloys LaB_6-$Me^{IV}B_2$, B_4C-$Me^{IV}B_2$ by diffusion welding method with intermediate barrier layers of powder thermoreaction mixtures (B-Ti-LaB_6) and crystals of euthectic alloys, and of manufacturing of cathode-heating knots, which consist of the ceramic current lead, of the heater from anisotropic graphite and emitter, and represent a continuous ceramic composite with geometric sizes of the functional elements: current lead -0,3x0,3x15 mm, heater - 0,3x0,3x1,5-2 mm, emitter - 0,6x0,6x2-3 mm. It is shown, that the high strength (σ_3>1400 MPa) and fractory toughness (K_{1C} = 24 MPa·$m^{1/2}$) of directly – crystalised boride ceramics allows to reduce sizes of the constructional elements up to a level of sizes metal (0.2-0.4 mm) and to save up their wholeness on a stage of manufacture and consequent maintenance in conditions of irregular high-speed heat - cool.

The miniaturization of a design in 2-3 times reduces power expenditures on heating of the cathode up to operation temperature, in some times reduces thermal loads on the constructional elements of an electron-beam gun in whole, so also magnitude of the thermal initiated strains last.

Besides the viscous ceramics on the base of of including boron refractory compounds with a majority of covalent component chemical bond, does not discover a noticeable high-temperature creep up to temperatures 0,5-0,8 T_m, that is much higher, than at metallic constructional materials (0,2-0,3 T_m) and does not reduce in a modification of the arrangement in space of an emitting surface of cathodes and violation of an adjustment of an electron-optical system of gears in process of their maintenance.

The directly heated cathode knots with lanthanum hexaboride emitter manufactured for gears of electronic - zond analysis, which show reproducibility and stability of heat performances as during manufacture from the cathode to the cathode, and on intervals of whole 500 hour terms of maintenance in vacuum 10^{-2} Pa. The cathode does not change the arrangement in space even at velocities of heat of 1000 grad\sec.

$LaCoO_3$-BASED CERAMICS AND ITS MECHANICAL BEHAVIOUR

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Mixed-conducting $LaCoO_3$-type perovskites are promising materials for solid oxide fuel cells and membranes for oxygen separation and partial oxidation of hydrocarbons, i.e., the equipment whose application can revolutionise the relevant technological procedures.

Extensive studies into perovskites have been performed but in publications almost no attention is paid to the mechanical behaviour of such materials though this is the factor that can control the possibility of their industrial application.

Using their own methods, the authors studied perovskites $La_{0.8}Sr_{0.2}CoO_3$ and $La_{0.8}Ca_{0.2}CoO_3$ manufactured by cold isostatic pressing with subsequent sintering [1]. Load vs., deflection curves were recorded and the above perovskites were found to be inelastic (relatively brittle) ceramics with different brittleness measure χ [2]. For $LaCoO_3$ $La_{0.8}Sr_{0.2}CoO_3$, and $La_{0.8}Ca_{0.2}CoO_3$ ceramics χ is equal to 0.7, 0.6, and 0.28, respectively. Residual strains are typical of this type of ceramics (Fig. 1).

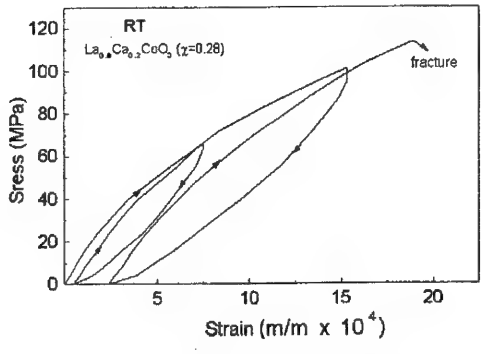

Figure 1. Stress vs., strain for perovskite $La_{0.8}Sr_{0.2}CoO_3$ under cyclic loading under conditions of 4-point bending at room temperature.

Unlike other ceramic materials [2], inelasticity of perovskites is related to the possibility of ferroelastic domains switch, which is characteristic of these ceramics. Performing high-temperature testing, we tried to establish the influence of Mott transition (dielectric – metal transition) on strength and deformability of the perovskites under study (Figure 2).

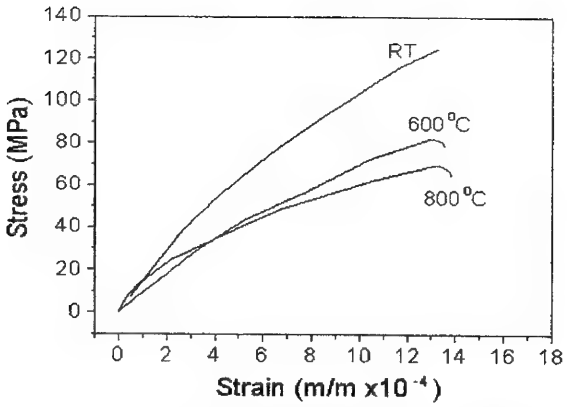

Figure 2. Stress and strain temperature dependencies for perovskite $La_{0.8}Ca_{0.2}CoO_3$.

In fracture toughness tests (Fig. 3) we tied to establish the temperature intervals of phase transformation and other effects governing the resistance of perovskites to crack growth resistance.

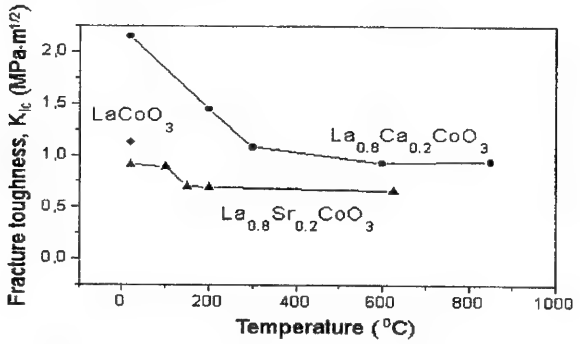

Figure 3. Fracture toughness variation with temperature for perovskites tested by the SEVNB method (3- point bending).

Using the data of fractographic, X-ray phase, and Raman investigations of the perovskites we analysed the results of the mechanical tests performed and formed a preliminary notion of the mechanical behaviour of these materials.

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CERAMICS FROM STABILIZED ZIRCONIUM DIOXIDE OF DIFFERENT FUNCTIONAL DUTY FOR THE METALLURGICAL AND OTHER BRANCHES OF INDUSTRY

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An intensification of technological processes in metallurgical, energetic, chemical and other branches, which determine the technical progress, requires a constant perfection of existing and making new high efficient refractory materials of different functional purpose.

One of such promising materials is zirconium dioxide the solid solutions of which with oxides of alkali-earth and rare-earth elements are characterized by high melting temperature, corrosion- and erosion resistance, low thermal conductivity, high strength and ion conductivity, good thermal shock resistance.

In the open joint-stock company "Ukrainian research institute of refractories named after A.S. Berezhnoy" as a result of carried out research the technology was developed as well as the production involving manufacture of a large assortment of products from high dense ceramics on the basis of ZrO_2 stabilized by Y_2O_3 or CaO. High dense products on the basis of ZrO_2+HfO_2 — not lesser than 92 %, CaO — within the limits of 4–5 %, Fe_2O_3 — not more than 0,2 % and open porosity — not more than 5 % are characterized by high resistance towards an action of different corroding agents, good thermal shock resistance and high heatinsulating capacity.

Crucibles, nozzles from zirconium dioxide stabilized by calcium oxide are used for laboratory meltings of non-ferrous and rare earth metals.

Electrolytic ceramic elements are solid electrolytes on the basis of ZrO_2 stabilized by Y_2O_3, with chemical composition of ZrO_2+HfO_2 — not lesser than 82 %, Y_2O_3 — within the limits of 15–17 %, SiO_2 — not more than 0,5 %, Fe_2O_3 — not more than 0,2 %, open porosity — not more than 0,1 %, apparent density 5,7 g/cm^3, specific electrical resistance at 1000 °C — not more than 20 Ohm·cm are characterized by high oxygenionic conductivity, gasproof, high resistance to an ageing ($R_1/R_0 \leq 1{,}05$) and they are on the level of best foreign analogues according to their properties.

Solid electrolytes on the basis of ZrO_2 stabilized by Y_2O_3 are produced as disks, capillaries as well as sheaths and pipes with a wall thickness 0,3–3 mm and they are used in hightemperature electrolyzes, sensors of gas analyzers and hygrometers.

PRODUCTS FROM STABILIZED ZIRCONIUM DIOXIDE FOR METALLURGICAL INDUSTRY

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A high metal resistance as well as corrosion and erosion resistance to the melt of liquid steel makes an employment of the ceramics from zirconium dioxide for the most responsible points of application in the metallurgical industry.

In the open joint-stock company "Ukrainian research institute of refractories named after A.S. Berezhnoy" as a result of carried out complex of research the manufacture technology of thermal shock resistant ceramics from ZrO_2 was developed. In partial the supports for heating highmelting alloys before the deformation up to 2000-2300 °C and sectors for the heatinsulation of the lining in induction furnaces withstanding more than 500 heats when heating these billets before the deformation were produced. The lining of induction furnaces with such sectors in. "Tube institute" operated more than 10 years. The properties of these products are following: chemical composition, %: ZrO_2+HfO_2 — 94,35, CaO — 4,33, MgO — 0,25, Fe_2O_3 — 0,09; open porosity — 23,2–30,2 %; apparent density — 3,91–4,27 g/cm^3. Non-swirl nozzles were produced which are used for casting in machines for casting of billets. They are not inferior to imported products and operate for a long time when casting metal with a constant rate of its efflux during the casting of a number of heats using the process "heat on heat". Indices of properties of inserts-non-swirl nozzles from electrofused ZrO_2 stabilized by MgO: chemical composition, % : ZrO_2+HfO_2 — 94,94–97,34, MgO — 1,5–2,5, Fe_2O_3 — 0,11–0,32, open porosity — 16 %, apparent density — 4,73 g/cm^3, cold crushing strength — 60,5 MPa, thermal stock resistance (1300 °C — water) — 2 heat cycles. Indices of properties of inserts-non swirl nozzles on the basis of electrofused ZrO_2 stabilized by CaO: chemical composition, %: ZrO_2+HfO_2 — 94,0–94,5, CaO — 3,6–4,0, Fe_2O_3 — 0,08, open porosity — 16 %, apparent density — 4,75 g/cm^3, cold crushing strength — 137 MPa, thermal stock resistance (1300 °C — water) —7 heat cycles.

The manufacture technology of crucibles from ZrO_2, stabilized by CaO for melting of platinum group metals with service temperature 2200 °C which replaced successfully imported products and they are used now by appropriate plants and organization for remelting platinum scrap. The ceramics for melting platinum is characterized by following properties: chemical composition %: ZrO_2+HfO_2 — 94,07–95,07, CaO — 4,5–5,4, Fe_2O_3 — 0,07–0,08, open porosity — 21,2–23,8 %, apparent density — 4,43–4,32 g/cm^3

LIGHTWEIGHT CERAMICS WITH A MICROPOROUS STRUCTURE

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A typical peculiarity of produced lightweight products is their high open porosity, which is formed at the expense of an introduction of foam forming or burning-out additives in the compound. In this case a prevailing size of pores inside of products is within the limits of 0,5–2 mm that determines their relatively increased thermal conductivity.

For the purpose of decreasing thermal conductivity of lightweight ceramics a new technological process was developed by authors which allows to shape a microporous structure of products when preserving high open porosity. The predominant size of pores is in the range of 0,8–5 μm.

On the basis of developed process two types of lightweight ceramics of anortite and calcium hexaluminate composition with the service temperature up to 1300 and 1600 °C are produced. The thermal conductivity is reduced by ~ 2,5 times compared with analogous lightweight materials produced in accordance with a traditional technology. At average temperature 650 °C the thermal conductivity is within the limits of 0,2–0,4 W/(m·K) depending on the composition of products. The cold crushing strength makes up 4–12 MPa at apparent density 0,8–1,3 g/cm^3.

Produced lightweight ceramics may be used not only as an excellent heatinsulator but it may find an application as filters for cleaning liquids and gases.

ELECTROTECHNICAL THERMAL SHOCK RESISTANT CERAMICS OF CORDIERITE COMPOSITION

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Owing to a electrical conduction, high electrical and mechanical strength as well as a capacity to withstand high temperatures the ceramics of cordierite composition is widely used in an electrotechnical industry.

The study was carried out and technological parameters for the manufacture of cordierite products with different types of refractory aggregates and magnesium containing components were worked-through.

It was shown that optimum relationship aggregate — cordierite binder is determined depending on the size, configuration and required properties of products. The cordierite content in products makes up 45–90 %.

The technological processes for the manufacture of cordierite ceramics using the pressing, drawing and thermoplastic casting under a pressure were worked-through. Cordierite products of different configuration and purpose produced at an institute have an open porosity 25–35 %, apparent density 1,8–2,0 g/cm^3 and cold crushing strength 35–60 MPa and high thermal shock resistance.

THE DEVELOPMENT AND PRODUCTION OF CORUNDUM CERAMICS

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In the open joint-stock company "Ukrainian research institute of refractories named after A.S. Berezhnoy" the technology of highdense ceramics (Al_2O_3 content not lesser that 99,5 %) and ultradence corundum ceramics (Al_2O_3 content not lesser than 99,5 %) is developed. This ceramics is modified by 0,15–0,20 % of MgO. Such ceramics possesses high mechanical and dielectrical strength ($\sigma_{bending}$ 180–250 MPa; $E_{strength}$ 18–20 kV/mm), vacuumdensity (limiting vacuum 1.10^{-10} Torr), chemical stability and resistance towards different types of abrasive action.

The manufacture principle of products from fine active to the sintering alumina oxide pastes at the temperature of 1750 °C without a participation of liquid phase was assumed as a basis.

The technological processes for manufacturing products of different configuration and sizes using a slip casting into gypsum shapes, an extrusion from plasticized pastes and thermoplastic shaping were developed. The compositions of plasticized binder were developed too.

For intricately profiled thin walled and precisely sized constructional elements of modern engineering the technology of cutting, grinding and polish of corundum products up to 9–10 class of the purity surface and an accuracy of specified sizes up to ± 0,05 mm, including on internal cylindrical surface with a length of 700 mm was developed.

The products from corundum ceramics are widely used in different branches of science and engineering: the sheaths for protection of electrodes of hightemperature thermotransformers, crucible for melting non-ferrous and ferrous metals and hightemperature glasses, insulators of intricate configuration, seal rings of water circled pumps, abrasive resistant elements of different units (nozzles, injectors) and others. Equally with a hightemperature use of such ceramics its employment as a constructional material is widened too.

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SURFACE TEMPERATURE OF GRADED CERAMIC HEATING ELEMENTS DEPENDING ON MICROSTRUCTURE OF RESISTIVE LAYERS

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Dense Si_3N_4 - ZrC composites with the ZrC phase in the range of 5 - 50 vol.% were produced by hot pressing technique in the reducing (CO). Two types of ceramic items in the form of the three dimensional component and the functionally graded material were evaluated. The influence of densification parameters, amount and grain size of ZrC particles and geometry of the functional zone on the microstructure, electrical resistivity was investigated. It was proved that the resistivity of electroconductive ceramics is strongly affected by the amount and morphology of the filling phase. An evident influence of the grain size distribution of ZrC powders and morphology of particles of the conductive phase on surface temperature heating elements was ascertained. Was showed possibility to 2 times energy saving if resistive layer of graded heating elements with coarse grains was achieved.

RESEARCH OF INFLUNCE OF TECHNOLOGY OF PREPARATION PIEZOELECTRIC CERAMICS OF THE $PbTiO_3$-$PbZrO_3$-Pb $(W_{1/2}Cd_{1/2})$ O_3 SYSTEM ON PHYSICAL PROPERTIES

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Piezoelectric ceramics on the lead zirconate-titanate (PZT) basis find more and more wide application due to the superior properties and stability to various external influences. The area of application of piezoelectric ceramics of the PZT system constantly extends and the requirements to such materials appreciably have raised. Therefore the problem of creation of the effective technological methods ensuring obtaining of high density ceramics with the improved and reproduced characteristics is solved first of all at development of new ceramic materials of various assignment.

The piezoelectric ceramics with high density are prepared by a method of hot pressing or method sintering of ceramics in oxygen environment now. Both those of methods are fairly complex and expensive. One of perspective methods for preparation ceramics of required density is the method of cold compacting with use of high pressure.

The purpose of the present work was the producing piezoelectric ceramics on the PZT solid solutions basis using various methods and research of influence of condition of preparation of ceramics on the dielectric and piezoelectric properties.

The researches were carried out on ceramic samples of the $PbTiO_3$-$PbZrO_3$-Pb $(W_{1/2}Cd_{1/2})$ O_3 system.

The parameters of crystalline structure researched ceramic were defined by the Rietveld method using the GSAS package. We studied the process of sintering of ceramics of the system PZT and the effect of high-pressure compaction on density, porosity and microstructure.

The piezoelectric and dielectric parameters of ceramic samples prepared at high and conventional pressures were determined. The temperature of sintering of ceramics of the PZT system reduces on 200÷250^{0}C has been established if the high pressure of cold compacting is used, at that the electrophysical properties conserve and the separate characteristics improve on 20÷25%.

STRUCTURE AND PHYSICAL PROPERTIES OF $PbTiO_3$ AND PZT CERAMICS PREPARED USING OF METHOD HIGH PRESSURE OF COLD COMPACTING

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The ceramics on the base pure $PbTiO_3$ is fragile and porous. As a rule, hard ceramics of high densety may be prepared by introducing certain amounts of various additives.

The present work shows the possibility of preparation ceramics $PbTiO_3$ and PZT with well reproducible properties and nearly theoretical density, using the method of high pressure of cold compacting (1 to 10 GPa). The results of investigations of peculiarities crystal structure and electrophysical properties of prepared by above mentioned method $PbTiO_3$ and PZT piezoceramic samples are presented.

Optimal conditions of preparation of high density ceramics samples with homogeneous structure are established on the basis of dilatometry (dilatometer D1-24 firm "Adamel Lhomargy") and thermogravimetry (firm "SETARAM" thermoanalyzer TG-92 16,18) methods. It is established by Rietveld method (GSAS package), that conservation of distortions crystal lattice (microstresses second of kind) take place for samples compacted by high pressure with following sintering. Values of microstresses and sizes of areas of coherent scattering are determined by using the method of second moments. The dependencies of these parameters on the pressure of cold compacting are studied. It is established that the temperature of ferrolectrical phase transition (FCPT) lowers monotonically if the pressure increases. The quantitative assessment of the width of FCPT is carried out on the basis of the theory of dither phase transitions and it is shown, that the lattice microstrains make the main contribution to the change of the transition width if the pressure 1 to 4 GPa are applied. It is established, that the use of high pressure of cold compacting of ceramic samples cause the decrease of displacement value of titanium ions in the crystal lattice.

Optimal technological parameters of preparation of в $PbTiO_3$ and PZT ceramic samples are determined. It is shown, that the application of high pressure at cold compacting of ceramics samples of 50 mm diameter and 15 mm thickness allows to bring down the temperature of annealing on 200 to 300 ^{0}C and to receive materials having density close to theoretical with improved electrophysical properties on 20 to 30 %.

RESEARCH OF INFLUENCE Bi_2O_3 ON PHYSICAL PROPERTIES OF A HIGH-FREQUENCY CERAMIC MATERIAL BASED ON BaO-Nd_2O_3-TiO_2

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Dielectric materials on the basis of ceramics are widely used in engineering of superhigh frequencies now .Dielectrics, which application essentially reduces overall dimensions of a microwave products (i.e. materials with high dielectric permeability) represent the special interest. The effect of miniaturization is based on reduction of length of an electromagnetic wave in dielectric in $\sqrt{e}$ of time. Dielectrics with high permeability are applied in engineering of a microwave as dielectric resonators, tie plates of microcircuits etc.

Dielectric ceramic materials should have both low dielectric losses and high thermostability. Therefore combination in the same substance high dielectric permeability and thermostability. is a complex scientific and technical task. The significant successes in this connection are achieved in complex oxides of rare elements.

The purpose of the present work was the research high-frequency dielectric ceramics based on BaO-Nd_2O_3-TiO_2, modified with Bi_2O_3 for increase dielectric permeability and temperature stability. In present work the researches on influence of the additive on modes of reception of ceramic samples, their physical properties and microstructure were carried out. The activation energy of sintering process of ceramic samples was determined and the influence on it of the additive Bi_2O_3 was investigated. The crystal structure of the received ceramic samples and the distribution of ions in sublattices of crystal structure were refined by the Rietveld method.

We have obtained that the introduction 0,2 up to 0,6 wt. % Bi_2O_3 raises dielectric permeability of a material on 10 - 15 %. The material has high Q-factor and temperature stability. The researches of microstructure have shown, that the received material has high density, porosity of samples does not exceed 1%. The introduction Bi_2O_3 in the specified range of concentration reduces temperature of sintering, that has important meaning for mass manufacture of products.

RESEARCH OF INFLUENCE OF TECHNOLOGICAL PARAMETERS ON MICROSTRUCTURAL AND ELECTROPHYSICAL PROPERTIES HIGH-FREQUENCY HOT-CAST CERAMIC MATERIAL

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The objective of this research was to design a technology for producing articles fully conforming to the current mast stringent requirements of large-scale production and displaying long-lasting operational reliability to provide overall cost-effectiveness.

Hot-cast ceramic based on lanthanum aluminate – calcium titanate served as samples. Using the method of mathematical experimental design the influence of technological parameters of hot casting, burning out the binder and firing the articles on the electrophysical and microstructural properties of ceramic material was investigated. Our experimental evidence on the microstructure, density and porosity of the hot-cast ceramic material are given. The influence of the type of the plasticizer , component concentration, regimes of burning out the softner and the firing regimes on the dielectric permeability, angle tangent of dielectric losses (quality factor), temperature coefficient of dielectric permeability over a broad temperature and frequency ranges has also been studied. Coaxial and cylinder dielectric UHF-, SHF- and microwave range resonators are produced. The data on the temperature dependent resonance frequency and quality factor of the resonators are presented.

Relying on the experimental data obtained we have designed the technology for producing high quality ceramic dielectric UHF, SHF and microwave range, resonators with high operating characteristics.

INFLUENCE OF HIGH PRESSURE OF COMPACTING (1-10 GPa) ON THE PROCESS OF RECEPTION, STRUCTURE AND PHYSICAL PROPERTIES OF THE MICROWAVE CERAMICS TiO_2-$Bi_2Ti_4O_{11}$

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In the given work is informed about the peculiarity of technology of synthesis and results of research of conditions of reception of the microwave dielectric ceramics TiO_2-$Bi_2Ti_4O_{11}$. A samples were synthesized from high-clean powders Bi_2O_3 and TiO_2 on air at the temperature 1150°C during 2 hours. Before annealing the samples were compacted by high pressure 1-10 GPa within 5 minutes. It has allowed to avoid use of plasticizer, to reduce temperature of sintering on 150÷200 °C and to receive ceramic samples with porosity less than 2 percents. X-ray analysis of the synthesis materials was carried out at room temperature in CuK_α monochromatic radiation. The conditions of formation of compounds were investigated on air with the help of thermoanalyzer TG-DTA-92 of the firm "SETARAM", and the process of sintering was studied with the help of DILATOMETER D1-24 of the firm "ADAMEL LHOMARGY" in an interval of temperatures 20÷1240 °C. The results of the analysis have shown, that the process of synthesis of researched compounds passes through formation of a lot of intermediate phases and is accompanied by losses of Bi at temperatures above 940 °C. Use compacting under high pressure has allowed considerably to reduce a losses of Bi in the process of annealing and to receive a material with a smaller deviation from stehiometry. With the help of isotermal and unisothermal methods of the thermal analysis and dilatometer measurements is investigated kinetics of process of sintering of ceramic samples compacted by high pressure and the meanings of activation energies of sintering are determined. The peculiarities of structure of compounds TiO_2 and $Bi_2Ti_4O_{11}$ contained in ceramic samples in depending from technological parameters and the pressure of compacting was determined by Rietveld's method, using GSAS program.

The researches of porosity and size of grains of ceramic samples on scanning electron microscope REM-100Y are carried out.

The data of measurements of dielectric properties of samples in an interval of frequencies 1MHz ÷ 3GHz and in a temperature range (–50 ÷ 150)°C are resulted. Is shown, that the received ceramic samples have high dielectric parameters (dielectric constant ε_r=80 ÷ 100, quality factor Q=1000 ÷ 1500, temperature factor of resonant frequency τ is close to zero.)

FEATURES OF OBTAINING CERAMIC HTSC SAMPLES BASED ON THALLIUM WITH APPLICATION OF HIGH PRESSURE

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The obtaining ceramic superconductors in systems containing thallium, is essentially complicated increased volatility of compounds with thallium both rather narrow temperature and concentration areas of thermodynamic and concentration stability of thallium based phases of superconductivity. It results that the development of technological methods of essentially reducing loss thallium during obtaining HTSC-ceramics gets the special value, both from the point of view of obtaining qualitative ceramic samples, and from the ecological and economic points of view.

The aim of work was development of technology of obtaining thallium-HTSC-ceramics with use of high pressure for compacting of source mixtures of oxides before synthesis and before annealing. The researches of technological features of obtaining single-phase HTSC of materials following series were carried out: $Tl_{(2+x)}Ba_2Ca_{(n-1)}Cu_nO_{(2n+4)}$ and $Tl_{(1+x)}Ba_2Ca_{(n-1)}Cu_nO_{(2n+3)}$, where n from 1 up to 6, and x varied from 0 up to 0,8 with step 0,2. The range used for compacting of pressure was (from 0,1 up to 8,0) GPa. The synthesis of HTSC-phases was carried out at temperatures 750°C and 800°C within 5 hours. Final annealing of ceramic samples passed within (from 1 up to12) hours at temperatures (from 800 up to 860) °C.

The methods TGA were used for investigation influence of source density of ceramic samples on loss thallium at various temperatures of synthesis and annealing. The complex temperature mode of annealing of ceramic samples were used. The temperature fast rose up to temperature close to temperature melting of a sample at which sample some minutes with the consequent fast cooling up to temperature of usual sintering were maintained. It carried out with the purpose of creation dense "crust" outside of a sample with the purpose of decrease of loss thallium at continuous tenacity.

The complex step modes of annealing with use of high pressure have allowed to receive single-phase superconducting ceramic samples with optimal electrophysical and structural properties and density close to theoretical. The specification of structure and the allocation of ions on nodes of a crystalline lattice were refined by the Rirtveld method using the GSAS package.

INFLUENCE OF THE MISMATH OF THERMAL EXPANSION COEFFICIENTS OF THE FILM AND SUBSTRATE ON THE ELECTROPHYSICAL PROPERTIES OF THICK-FILM RESISTORS ON THE BASE OF SnO_2 - Sb.

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One of important problems in modern microelectronics is the development of resistive thick-film compositions on the base of cheap and accessible materials, and searching for a method of management of such composition properties. The thick-film resistors consist of a glass dielectric matrix, which provides consolidation of a film and its adhesion to the substrate, with the particles of a current-carrying phase dispersed in it. On the development and investigation of the thick-film compositions, there exist problems with the interrelation between the thermal expansion coefficient (TEC) of composition constituents, and between TEC of the film and substrate. The mismatch between these coefficients results in the residual thermal stresses, which affect electrophysical properties and operational parameters of the resistive films.

Earlier, we have investigated the influence of the mismatch of TEC of constituents of cermet films on the base of SnO_2 - Sb solid solution, which are known as perspective materials for superhigh-ohmic resistors. The influence of TEC of the substrate on the resistive film properties is not yet investigated. The investigation of such influence on the properties of these compositions is especially important because of its high gauge factor due to predominance of the tunnel mechanism of electrical conductivity.

The electrophysical properties of films on the base of SnO_2 - Sb on the substrates (ceramic, glass ceramic, metal) with different values of TEC are investigated.

The interrelation between the residual thermal stresses due to mismatch of TEC of the films and substrates and electroresistance of the compositions and temperature coefficient of resistance is established. The physical aspects of this interrelation are discussed. The results of calculations and experimental data considered in the framework of the offered model of the influence of residual thermal stresses on electrophysical properties of the films with predominance of the tunnel mechanism of electrical conductivity.

THE INFLUENCE OF LASER IRRADIATION ON ELECTROPHYSICAL PROPERTIES OF THICK FILM RESISTORS (TFR) APPLIED TO CERAMICS SUBSTRATE 22XC OR BK94 TYPES

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Technical ceramics is widely used in microelectronics when creating integral devices. It is multy–functional material and it must conform to the fixed (electrophysical and mechanical) requirements.

Considered in the paper is the application of technical ceramics for making TFR on the base of borides of transition and alkaline earth metals. The influence of pulse laser irradiation ("Kvant–15" plant) on electrophysical properties of TFR applied to the ceramics substrate 22XC or BK94 types was investigated. When treating TFR with laser irradiation the initiation of high thermal gradients is possible. These gradients may result in wrecking of substrate materials, therefore, conditions of laser treatment with previous heating of resistor were selected. Radiographical investigations of TFR material applied to the ceramics substrate were carried out.

Energy of laser irradiation was varied from 0.5 to 2J. Surface morphology was stadied with the method of atomic force microscopy (AFM).

ELECTRICAL CONDUCTIVITY OF PYROCHLORE SOLID SOLUTION BASED ON $Ln_2Zr_2O_7$

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There is a considerable interest in rare-earth zirconates ($Ln_2Zr_2O_7$) because of possible application as fuel cell electrolytes materials, high-temperature heating elements, oxidation catalysts, host materials for fluorescence centers, thermal barrier coatings. The pyrochlore crystal structure of these compaund is unique. It allows numerous ionic substitutions at various lattice points, producing many phases with different thermal, electrical and catalytic properties [1].

Our aim is to study the influence of both cation and anion vacancy ordering on electrical properties of $Ln_2Zr_2O_7$ (Ln = La, Nd, Sm, Eu, Gd) based phases. Of special interest is to conductivity behaviour in the visinity of the stoichiometric pyrochlore composition. Point defects (oxygen vacancies or interstitials) was introduced by substituting Ln^{3+} or Zr^{4+} on Ca^{2+} or Y^{3+} ions, respectively, in the stoichiometric pyrochlores. Non-stoichiometric compositions can be considered as stoichiometric compounds doped with one of the end members of the ternary systems ZrO_2-Ln_2O_3-CaO (Y_2O_3).

Ceramic and hydrothermal techniques were used to prepare powders of pyrochlores and solid solutions. X-ray diffraction of sintered specimens showed no second phases.

The temperature dependence of electrical conductivity was registered in the temperature range 600-1300 K in air. The measurements of conductivity were made from DC to 30 kHz. The ionic portion of conductivity evaluated by the polarisation method. For a given level of dopant the substitution of Ca^{2+} for Ln^{3+} gives significant increases in specimen ionic conductivity.

1.Electrical properties of phases in the ZrO_2-Y_2O_3-La_2O_3 system / A.V.Zyrin, A.V.Shevchenko, L.M.Lopato // Powder Metallurgy and Metal. Cer.-2000.-V.39,№3-4.-p.146-160.

RESEARCH OF AN ELECTONIC STRUCTURE OF PYROCHLORE CERAMIC MATERIALS BY X-RAY AND X-RAY PHOTOELECTRON METHODS

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The study object were the ceramic materials based on $Ln_2Ti_2O_7$ (Ln=Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, Lu). These refractory substances having a pyrochlore-type structure, possess a high dielectric constant and used in a number of areas of modern engineering .

In this work OKα X-ray spectra (XRS) and X-ray photoelectron spectra (XPS) of valence band (VB) and core levels were obtained in titanates $Ln_2Ti_2O_7$ and also, for a comparisin, in titanium dioxide.

Is shown, that the OKα-band shape and width, describing O2p-electrons distribution in substances VB are changed a little for all number of titanates. The Z_{Ln} increase calls some changes of OKα-spectra fine structure, which reflects features of O2p-electrons distribution. The features intrinsic to this distribution in TiO_2 are exhibited in titanates also. The VB XPS of $Ln_2Ti_2O_7$ reveal characteristic features of their electronic structure as a whole. Is shown, that the VB is not less than 22 eV and is close to 24 eV. VB consist of two subbands, which structure depends on Z_{Ln} . In the upper subband Ti d,p-, O2p-, Ln4f- and valent electrons are concentrated. The lower subband contains O2s-, Ln5p- and Ti p(valent)-electrons. The natural changes in titanates electronic structure are detected. The Z_{Ln} increase essentialy will transform both VB subbands. The increase of an amount of REE 4f-electrons noticeably changes the shape and increases the upper subband spectrum intensity.For want of it the sequential displacement of a subband connected to Ln5p-electrons to the VB botton happens. In $Lu_2Ti_2O_7$ Lu5p-electrons spectrum falls outside the VB spectrum boundary, and the upper subband spectrum is sharply narrowed down for want of increase it of intensity. XPS of core levels show, that the covalevce degree of Ti-O bond in titanates is higher than in TiO_2 .

STRUCTURAL ASPECT OF FORMATION OF $CrSi_2$ RESISTIVITES THIN FILMS

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Chromium disilicide thin films can be widely applied as resistant, contact layers in the integral circuites.

The films were prepared by the ion-plasma method sputtering chromium disilicide targets, produced by hot forming powder $CrSi_2$.The residual gas pressure was about $1x10^{-4}$ Pa, and the pressure of argon during deposition was $4x10^{-2}$ Pa. At a target voltage of 1kV and a target current of 50mA, the film thickness was 10-100 nm.

To investigate the structure by transmission electron microscopy, the films were condensed on (100) surface NaCl, from which they were separated by distilled water and supported by grids of copper or molybdenum. Resistivities were calculated from the sheet resistancy, measured with a foir-point probe. Films deposited at T_s = 333 K are amorphous. The transmission electron micrograph shows a fine – grained contrast which is typical of amorphous structures. It is shown, that films deposited on the substate at T_s = 573 K have amorphous and crystalline phase.

Linears, volumes and configuration parameters of crystalline and amorphous phase of microstructure production on transmission electron microscope of $CrSi_2$ thin films are studied using computers analysis of image. Linears dimension of crystalline phase and its spesific number are dtcrease with the growth of films thickness. Evolution of microstructure from matrix to matrix – statistic type is happen stipulate recrystallization effect in the process of film setting, coalescence isolated standing by crystalline and "caking" of contacting particles.

Thermal and corrosion stability, thermal stability of the parameters and also small temperature electric resistivity coefficient make chromium disilicide thin films perspective in the microelectronics as a contact layers with low temperature electric resistivity coefficient.

THERMOELECTRIC PROPERTIES OF SEMICONDUCTOR CERAMICS

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It is known that composite and ceramic systems composed of the following phases: semiconductor – metal, semiconductor – semiconductor, semiconductor – dielectric, metal – dielectric, show semiconductor and semi – metal properties. Such materials were named "unhomogeneous semiconductors". They have a number of specific pecularities such as temperature and mechanical stability,availability of more factors by means of which the material characteristics and technology can be controled and changed.

One of the problems on the development and investigation of the materials is to jind out concentration and temperature dependences of their thermoelectric properties and methods for optimization of the strucnural and technological factors responsible for these properties.

The authors have developed a new effective model for the electrotransfer through ceramic and composite particles connected both in series and parallel. Using the model in the analysis of the thermoelectric properties of the $(1 - x) CrSi_2 + xNi_3B$ system (semiconductor – intermetallide) permitted the separate contributions of the two phases into the electrotransfer in the material to be determined. Some results of the analysis are shown in the table.

T a b l e. The concentration and temperature dependences of the thermoelectric properties of the $(1 - x) CrSi_2 + xNi_3B$ composite and its phases.

		Composite		Phase"A" ($CrSi_2$)		Phase "B" (Ni_3B)	
T,K	x,volume fraction	ρ, Ω cm	α, μV/K	ρ_a, Ω cm	α_a, μV/K	$\rho_в$, Ω cm	$\alpha_в$, μV/K
523	0,1	7,0	100	10	320	1,4	26
673	-"-	3,4	117	7,0	293	1,6	52
523	0,3	2,0	–23	4,8	65	0,1	–36
673	-"-	0,8	– 4	2,7	88	0,3	–21

Here: ρ – electrical resistiviti, α – thermoelectric coefficient.

Besides, the internal parameters of the electrotransfer in the phases were calculated. The mechanism of formation of semiconductor and metallic types of conductance was determined.

SOLID-STATE REVERSIBLE REACTIONS OF THE $MgO-Al_2O_3-SiO_2$ SYSTEM AND CONTROL OVER THE PROPERTIES OF CERAMIC CATALYST CARRIERS

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The mechanism of the solid-state reversible reactions in the $MgO-Al_2O_3-SiO_2$ system has been studied. During the study, the basic stages of these reactions and temperature conditions of their conjugate bond have been revealed. The reaction conjugation determines the auto-catalytic nature of the interaction while inhibited according to the principle of negative back bonding. Such interaction considered to be very promising for the advanced ceramics synthesis as the changes of the material temperature lead to the forming of several quasi-equilibrium states between various phases that are characterized by their maximum response toward essential gradients of external heat flows without destruction of material. Such materials are characterized by a high thermal stability as their structure and phase compound can be flexibly adapted to the changes of the environment not only due to the efficient heat dissipation to the environment, but also due to the additional heat consumption for the solid-state reversible reactions.

In our analysis, we consider the example of making ceramic materials for catalyst carriers, i.e. such products like "handwheel" and methane reforming processes. It was demonstrated that the pore space of materials can be directionally organized due to the changes of volume during the solid-state reversible reactions, which allows to restrain or completely eliminate the use of ecologically hazardous burning-out mixtures. The reactive nature of baking enables one to obtain the required strength characteristics and, in the synthesized materials, to restrain the share of glass phase which can actively interact with the catalyst and poison them.

We have analyzed the effect of additional reinforcement and control over the phase compound of material during the phase decay of sapphirine and cordierite solid solutions after the spinodal mechanism. This effect occurs due to the forming of high-disperse, heterogeneous, coherent system of elastically matched, spatially disoriented crystalline gratings of different phases.

MAKING OF CERAMIC TARGETS FOR MAGNETRON SPRAING

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In given work the method of making of alloyed yttrium chromite and modified zirconium dioxide ceramic targets for magnetron spraying of coatings have been studied.

The methods of hot and cold pressing of powders alloyed yttrium chromite $Y_{0,9}Zr_{0,1},Cr_{0,8}Al_{0,2}O_3$ (mass.%; $57Y_2O_3$; $34Cr_2O_3$; $5,6Al_2O_3$; $3,4ZrO_2$) and modified zirconium dioxide ($92\%ZrO_2 + 8\%Y_2O_3$) was tested. for making of targets with diameter 60-100 mm and thickness 4-8 mm

A method of hot pressing in graphite form allowed to make the samples with very low porosity (2-3%), but with impurity of carbon and products of his interaction with oxides of ceramic (chromium and zirconium carbides) during baking. Presence of these impurities leads later on to worsening of coating quality. For removal of this influence a method of cold pressing of. targets was tested.

Technology of making of targets by this method includs a cold pressing and following high temperature baking. A chemical clean and micron grainy chromium, yttrium, zirconium and aluminium oxides was used as burden materials. The 15 % water solution of polyviny alcohol was plasticizer in amount 3-5% from weight burden. A cold pressing of targets was carried out under pressure 80-100 MPa. Obtained samples were heated together with furnace in environment of air at the temperature 1073 K for full removal of moisture and alcohol with next cooling to room temperature. Baking was conducted in environment of argon at the temperature 2023 K during 4 hour. for yttrium chromite and 1823 K during 2 hour for zirconium dioxide.

After baking an alloyed yttrium chromite has a crystalline grating near to ASTM standard (a = 5,241Å, b = 5,521Å, c = 7,533Å) and the modified zirconium dioxide - tetragonale T - phase.

Obtained in this way targets have porousity up 15-25 % and be not contaminated by undesirable outsider impurities.. Quality of obtained targets provides spraying of coatings with necessary thickness and given composition.

Synthesis of nanocrystalline barium titanate powders from barium titanyl-oxalate: influence of process conditions on mechanisms and synthesis routes.

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Change of mechanisms acting on thermal decomposition of barium titanyl-oxalate, and therefore the structure of intermediate products, defines the physicochemical properties of the final barium titanate powders. The thermal decomposition process must be undergone control providing the optimized nonisothermal regime resulting in nanocrystalline barium titanate powders of high stoichiometry without barium titanate impurities. This paper presents the results of thermal decomposition of barium titanyl-oxalate under different heating rate regimes in different media: in vacuum (P = 133,3 Pa); in the air streem removing the gaseous products of decomposition from the reaction zone; in the non-isolated system in the ambience of the decomposition products. The methods of thermogravimetry, infrared spectroscopy, radiospectroscopy and x-ray phase analysis were used. The possible routes of precursors' thermal decomposition are shown and the optimal regime of synthesis is offered, which results in nanocrystalline barium titanate powders of the best properties.

PRODUCTION AND ELECTROPHYSICAL PROPERTIES OF THE THICK FILMS ON THE BASE OF HEXABORIDES BaB_6 AND LaB_6 MICROCOMPOSITE POWDERS

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Thick films having powders of BaB_6–LaB_6 solid solutions as the electroconductive phase and glassy materials as the dielectric matrix have found wide application in the resistor–building. In many respects electrophysical properties of the films are determined by the surmount mechanism of energy barriers with the carriers. These barriers are dielectrical interlayers between the particles of current–conductive phase in the films structure that are forming in the process of their heat treatment.

In order to investigate the effect of the dielectrical interlayers on electroconductivity of the thick films the microcomposite powders of metal hexaborides were synthesized. They are the particles of current–conductive phase with preapplied glassyphase layer of adjusted thickness (2.5 – 7.5 nm). Application of glassyphase layers to hexaborides powders was carried out from the water solution of *Ba*–, *Al*–acetates and with borid acid too.

Thick films were obtained by the method of stencilled printing followed by heat treatment. Examined in the paper were electrophysical properties of the films both on the base of microcomposite powders and starting powders of BaB_6–LaB_6 hexaborides with the different content of glassyphase. Proceeding from the developed structural model thicknesses of dielectrical interlayers between particles of current–conductive phase were calculated for both types of the films. We revealed correlation between electrophysical properties of the films and thicknesses of interlayers.

The influence of previous application of oxidic layers to the particles of current–conductive phase powder on electrophysical properties of the films was found to be conditioned by the following factors:

- protection of current–conductive phase from oxidation when heat–treating the films;
- lack of direct electrical contact between particles of powder;
- change in thickness of dielectrical interlayer in the film structure;
- evener distribution of current–conductive particles in dielectrical matrix;

CONSTRUCTIVE CERAMIC GOODS UNDER PRESSURE

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Creation constructive ceramic goods, such as deeffence covers for submarine device, needs experimental dates of strength and stability under pressure. These dates were determined due to academicion G.S.Pisarenko found and according to optical-polarise and mour stripe methods, [1].

Extremal means of strength under one exis pressure σ_c and selective coefficient of variation,υ% for cylindrical specimen, diameter 10 and heigh 30 mm are presented in table.

Material	σ_c, MPa	υ, %	Material	σ_c, MPa	υ, %
Glass 13B	2250	9,4	Porcelaine electr.	1278	8,3
Gl.quartz КУ	3200	6,5	Stone casting	1230	10,3
Sytal СТЛ-10	2702	3,8	Boron carbide	4264	-
Sytal АС-37	2778	5,1	Silicon carbide	2486	7,4

Affect constructive-technological and operetional factors, such as influence coefficients $\gamma_1, \gamma_2, \gamma_3, \ldots \gamma_n$ on meaning external state $\sigma_{гр.}$, were estimated in [2]: $\sigma_{гр} \sim \gamma_1 \cdot \gamma_2 \cdot \gamma_3 \cdot \ldots \cdot \gamma_n \cdot \sigma_c$. Here, influence staine stage, in third quadrant coordinate plane, and specimens dimentions are estimated by strength criterions under two-exis presure, [3] brittle materials and by Vabules formula. During m cycle of presure, influence coefficient γ_u and strength boundary σ_u are connected by function [2]: $\gamma_u \sim \sigma_u/\sigma_c = (1 - 0.065 \ln m)$.

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WEAR-RESISTANT MATERIALS BASED ON THE SYSTEM "BN-METAL OXIDES"

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A range of multicomponent materials based on hexagonal boron nitride, silica, alumina and zirconia was developed to work under friction and mechanical load conditions and also in aggressive media within a wide temperature range.

The materials have been obtained by means of hot pressing. The developed technology allows formation of structures having evenly distributed solid refractory fine-grained phases that determine high mechanical properties and efficiency under conditions of intensive wear in color metal melts.

Some mechanical and physical properties of the materials in question are given in the table.

Table

Properties	BN	BN-SiO_2, Al_2O_3	BN-ZrO_2
Density, g/cm^3	1,95-2,05	1,7-2,0	2,7-2,95
Hardness Vicker's, GPa			
perpendicular	-	1,5	1,5
parallel	-	1,3	1,3
Compressive strength , MPa			
perpendicular	315	370	362
parallel	230	317	324
Elasticity modulus, GPa			
perpendicular	32	69,7	70,5
parallel	6	64,3	70,8
Conductivity coefficient, W/ mK, 20 C			
perpendicular	31	36	40,2
parallel	18	20	22,6

SOFT MAGNETIC COMPOSITION WITH CERAMICS LAYERS

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The high specific magnetic losses confine applying powder soft magnetics of materials by operation in a variable magnetic field. The reduction of losses by currents and, hence, of total magnetic losses is possibl by creation of a laminar material with ceramics by interlayers.

In work the results of exploration of conditions of reception laminar soft magnetics of materials with ceramics interlayers are reduced. Influence on their magnetic properties of thickness of a sample, makeup and amount electrical insulating of interlayers.

As an ingoing material used an iron powder of the brand ПЖР 3.200.28 Brovary of a production plant of a powder metallurgy and ceramics interlayers.

The magnetic properties of obtained materials in a variable magnetic field are learnt.

Is rotined, that a magnetic induction and the specific magnetic losses are inflected depending on thickness of a magnetic conductor, makeup and amount a ceramics interlayers.

The creation of a slaty structure allows to adjust the magnetic characteristics of a material.

Ground of experimental data the analytical dependences of the base magnetic characteristics are obtained. At the specification statement of magnetic properties of magnetic conductors production materials in a class of exponential functions it is possible in an indiscrete kind to receive their mathematical expressions in a wide range range of magnetic density, thickness of a magnetic conductor and amount ceramics interlayers.

So, for example, the dependence magnetic induction from magnetic density frequency 50 hertz looks like:

$$B=K\cdot\{1-Exp[-0.0013\cdot(H-30)]\},$$

where coefficient K depends on thickness of a a magnetic conductor, makeup and amount ceramics interlayers.

INCREASING OF EFFICIENCY OF USING OF NATURAL GAS

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For today in Ukraine the plenty of natural gas on thermal power stations with low efficiency is used. As is known, the natural gas concerns to irretrievable natural resources, with which in due course will be absolutely exhausted. Therefore for all states of the world any attempts of economy of gas are by a urgent task.

Efficiency of using of natural gas on thermal power stations, as a rule, small (the efficiency makes 0,05-0,1). While at application of natural gas in electrochemical generators with solid oxide fuel cells (SOFC) it is possible to reach efficiency =1.

For today during using SOFC, it was possible to reach efficiency of using of natural gas 0,45-0,6 (www/dodfuelcell/com/solidoxid/html).

The increasing of efficiency of using SOFC today is caused by large difficulties:

- first of all it is their manufacturing;
- high prices.

The manufacturing is complicated due to the rigid requirements to their manufacture:

- The reception of disporous layer of ceramic electrolyte by thickness is close to 100 microns;
- The drawing from both sides of thin layer (close to 50 microns) anodi and katodi material with the large specific surface (close 100 $м^2/g$);
- Drawing an intermediate layer for increasing the durability of coupling between the electrolyte-cathode and electrolyte-anode, and decrease of influence of various factor of thermal expansion at heating a fuel element to working temperature up to 1000^0 C.

Thus, using of strong-fuel elements and increasing of efficiency of their work leads to reduction of pollution of an environment, improvement of quality of life and health of the population.

INFLUENCE of ACTIVATORS of SINTERING ON DIELECTRIC PROPERTIES of HOT-PRESSED BN CERAMICS.

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High electroresistance, low significance of dielectric losses, kept in a wide range of temperatures and frequencies, high stability to termostresses, makes BN ceramics a material suited for application as high-temperature dielectric first of all for gradient ceramics. The electrophysical properties of BN as individual connection are investigated rather well, however electrophysical properties of BN ceramics, which is geterophase material with the additives of activators of sintering are investigated unsufficiently.

The purpose of this work is the research of influence of the additives on dielectric characteristics of BN hot-pressed ceramics.

We have studied frequency dependence of ε and temperature dependence of conductivity of the synthesized BN samples with the additives MgO, Al_2O_3, Nb_2O_5, Y_2O_3, ZrO_2.

It is established, that the depth of dispersion (D) of ε in the range of frequencies 1kHz - 1MHz is grows, and the energy of activation of conductivity (Ea) in a range 300 - 500^0 C decreases on a number of the additives MgO-$Y2O_3$-ZrO_2-Al_2O_3-Nb_2O_5 (Tab. 1). The correlation between depth of dispersion of ε, energy of activation of conductivity and ionocity (I) of secondary formations Me-B and Me-C is also observed.

Table 1.

Additve	MgO	Y_2O_3	ZrO_2	Al_2O_3	Nb_2O_5
D	0.05	0.09	0.1	0.14	0.15
E_a eV	0.25	0.18	0.11	0.05	0.03
I, %	14.79	14.79	8.6	6.06	3.92

From the analysis of the received results follows, that the physical properties of ceramics on a basis BN defined by structure of grain-boundary phase, greatest temperature stability of physical properties have composites with the additives of MgO and Y_2O_3, the same materials have also greatest frequency stability of dielectric characteristics, and therefore, smaller defectivity of grain-boundary phase.

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PRACTICAL MODELING OF STRUCTURE AND PROPERTIES OF CERAMIC PRODUCTS USING INDUSTRIAL BY-PRODUCTS

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Properties of the building ceramic products of wide range are determined by the parameters of crystal structures, which are formed during burning process.

Based on the carried out research and tests, major directions of practical modeling of structure and properties can be outlined:

- Optimal proportioning of the major rock-forming minerals in the mixture of kaolinite, hydromicaceous-kaolinite and multi-mineral clays. Rational proportions of Ukrainian natural clays as mixture basis were determined;
- Mixture doping by the substances with genetically developed crystal/vitreous phases. Raw materials of both natural (basalt, stone crusher screenings) and industrial origin (metallurgical slag, red mud at alumina plants) were determined, which contain anortite, wollastanite, cristobalite, haematite and quartz in their crystal phase. Together with formation of similar crystals during burning of clay components and mullite, this enables to expand modeling ability of products' structure parameters with simultaneous reduction of power consumption;
- Using of mineralizing additives to intensify phase transformation and sintering. Experimental proof was given for the efficient use of manganese and copper oxides and sodium/calcium/lithium fluorides as mineralizing additives during fast burning (40-60 min at 1000-1100°C max.), and some trial processes were tested using electroplating and ferroalloy industry by-products as mineralizing additives.

The above approach was applied to the ceramic tiles production processes, namely:

- fast burning process of low-shrinkage wall tiles at the flow conveyor lines, using granite/syenite screenings and metallurgical slag;
- hardly sintered floor tiles, using industrial by-products as mineralizing additives;
- acid-proof materials, heavy-duty and alkali-resistant pipes.

PROCESS MODERNIZATION AND PROPERTIES IMPROVEMENT OF DECORATIVE CERAMICS AND PIPES

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Practical implementation of basic 'composition/structure/properties' model of material science is given in this article with regard to the processes of decorative ceramics and pipes.

Ceramic mixtures based on clay of varying mineralogical type with addition of grog and granite/syenite screenings, which could be used for products' manufacture by plastic molding, were examined herein.

Possibility to control the parameters of cross-linked macrostructure, characteristic for ceramic materials, was shown by experiment with the aid of packing factor improvement in the solid phase by pores and thinning agents' dispersion.

Possibility to control the parameters of cross-linked macrostructure with the aid of microcracks' healing by liquid phase exposure (A.F. Ioffe effect) was shown by experiment. Liquid phase is formed during burning of the above-mentioned mixtures together with granite/syenite screenings, which act both as thinning agent while molding/drying stage and thinner/flux while burning stage, because of the increased content of alkaline and alkaline-earth metal oxides.

Possibility to control crystal/vitreous phase relation in the burned products, depending on the granite/syenite screenings concentration, degree of dispersion and maximum burning temperature within 1150 - 1250°C was established. Some peculiar features were noted in the qualitative content of crystal phase to be formed, represented by quartz-cristobalite-mullite-anorthite-haematite system.

Structural change of the burned samples determines improvement of their physical/ mechanical properties and performance, namely reduction of water absorption, density growth, strength and chemical durability increase.

This research has resulted in modernization of plastic molding process parameters: rational proportioning of clay and thinner/flux, preparation of thinner/flux of the predefined dispersion degree and its homogenous blending with clay components, and optimal burning mode at the reduced temperature.

INVESTIGATION OF MECHANICAL PROPERTIES AND PHASE TRANSITIONS OF MULTIPLAYER CERAMICS MATERIALS OF THE PZT TYPE BY INTERNAL FRICTION METHOD

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Multieffective piezoceramics materials are multiplayer solid solutions received on the base of the $PbTiO_3$-$PbZrO_3$ type solid solution, which name is PZT. Physical properties of these materials depend on chemical composition, technological process, domain structure as well as real structure.

In investigations of the real structure of pottery-materials, the method of internal friction has been used lately more and more often. It permits to obtain very essential conclusions about microstructure and its changes based on observation of macroscopic mechanical of a sample twitches. Use of the internal friction method in investigations of pottery-materials leads to improvements and optimization of technological process, receiving materials with optimum, and compactly definite properties, investigations of phase transitions, qualifying mechanisms responsible for their special properties, and also to widening possibilities of use in modern technics, medicine and electroacoustic.

The aim of the work is to present results of the investigations of multicomponent ceramics of the PZT type, which were obtained by means of automatic acoustic frequency relaxator. The relaxator made it possible to investigate internal friction phenomena and changes of the Young modulus. Measurments of the temperature dependences of internal friction made it possible to qualificate temperatures of occurence of phase transition from ferroelectric rombhoedrical to tetragonal, and also from ferroelectric to paraelectric phase (Curie temperature). These measurments contributed to observe processes connected with change of domain structure and domain wall mobility.

FERRITE MATERIALS FOR TVT APPLICATIONS

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In television tubes (TVT) the major purpose of the ferrite core is to amplify the effective magnetic field, to enable magnetic deflection to take place under standard operating conditions. In the deflection system, 2 pairs of coils, aligned at 90◦ to each other, are used to deflect the electron beam horizontally and vertically. One pair of coils may be wound directly on the ferrite core, or both coil pairs may be remote from the ferrite; hence the terms direct or indirect winding are used to describe the application.

Approx. 80% of the products required by the World-wide market are manufactured in the region of Asia Pacific. All major ferrite product suppliers manufacture their own powder grades; product and powder manufacture are generally carried out at the same location, in order to realise economies of scale.

A brief description of the application is given, followed by an overview of current market requirements for TVT, and the implications for the deflection systems and for the ferrite core. Commercial ferrite grades are primarily based on two families of materials, namely magnesium zinc ferrites and manganese zinc ferrites, both of which are sintered and cooled entirely in air. The processing of these materials, from raw materials to ferrite powder production, for subsequent pressing and sintering are reviewed. The relationship between magnetic/mechanical/physical properties, and microstructure development/ferrite composition are discussed. Finally, future trends towards higher performance materials for higher application frequencies are reviewed.

THE DIELECTRIC PROPERTIES OF ALUMINA/POLYPROPYLENE MATERIALS

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Composites made of ceramic particles embedded in polymer matrix are at present recognized alternative to traditional ceramic materials for an array of applications. The materials are useful in design of capacitor and electric energy storage devices, pyroelectric sensors and ultrasonic transducers, due to their unique combination of mechanical flexibility and low processing temperature with special electric, optical, magnetic and insulate properties [1, 2].

The design of ceramic/polymer composites with low dielectric loss in a wide band of frequencies for electronic devices is an important problem.

Based on fundamental theories and recent developments, the system polypropylene/ Al_2O_3 is fully examined and discussed.

Experimental data on the dielectric permittivity and the dielectric loss of pure polypropylene and 0-3 polypropylene – Al_2O_3 composites with volume fraction of ceramic to 0.42 are presented. The volume fraction was determined using thermogravimetric analysis. The dielectric characteristics were measured using a strip transmission-line field applicator [3] with an HP 8720B in the frequency range 2 GHz to 18 GHz.

Samples of the composites were fabricated by mixing up alumina powder A1000SG (Alcoa) with polypropylene homopolymer flake resin Pro-fax 6501 (Basell) using auger-type extruder then extruded, cooled and cut the composite on small parts (pellets). The composite plates were prepared by pressing the pellets and finally specimens were prepared by milling to necessary shape.

It is shown that the relative dielectric constant of the composites increase up to 4.1 with increasing of ceramic volume fraction to 0.42 in accordance with theoretical prediction and is stabile over the operating frequency band. The dielectric loss keeps low value over the studied range of frequencies.

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FEATURES OF CHANGE OF STRUCTURE AND PROPERTIES HYDROHYAPATITE AT SINTERING

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In the given work the conditions of formation of hydrohyapatite powder pressings in process of sintering both evolution of their structure and properties are investigated with the purpose of reception of dense ceramics with the acceptable functional characteristics. The initial powder synthesized by precipitation from a water solution was used. According to x-ray researches, the chip sizes of a powder were from 200 up to 300Å. By pressing under pressure 100MPa received briquettes of the cylindrical form of the various sizes, and also as rectangular prisms of square section. The pressings calcined within one hour at temperature 500^{0}C in certain environment, then annealed within two hours on air at more temperatures in an interval from 600 up to 1400^{0}C. Heating and cooling made with rate of 12deg/min. At smaller rate of heating final porosity of ceramics it appears large, and at higher rate - there are cracks in it.

On curve of particle size distribution for samples, annealed up to 1150^{0}C, there is mainly one maximum. At increase of annealing temperature on curve distribution in the field of the large sizes some smaller maxima are fixed.

The activation energy of process of chips growth has appeared 27 кcal/мol, that is close to found earlier. The small value of activation energy, apparently, reflects fact, that the delivery of a material for chips growth is carried out through a gas phase, and its source are the rests of a amorphic language hydrohyapatite fraction of a powder, which is kept in samples up to 1400^{0}C.

The shrinkage pressings process is finished practically at temperature 1250^{0}C. In temperature range of 600-1250^{0}C the average size of areas coherence scattering is increased. Thus the stochiometric composition of chips comes nearer to theoretical and their crystal structure is improved. At annealing temperatures more 1250^{0}C stoichiometry of hydroxyapatite ceramics is a little worsened, the areas of coherent scattering decrease in the sizes, though the maximal sizes of chips are increased.

Density of sintered ceramics has made 99 % from theoretical density (p_{theor}=3.16 g/sm^3), microhardness Hv=600 kg/mm^2, compressive strength σ =450MPa.

SOME SINTERING PARTICULARITIES of HYDROXYAPATITE POWDERS

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Hydroxyapatite (HA) is the fundamental mineral component of bone tissue. The materials on a HA basis for medical applications are usually made as coating on metal and both granules and bulks form with variations in porosity. The special interest is represented porous HA ceramics, however, the weak mechanical properties of these bioceramics have been the primary obstacles to their applications for bone defects filling, which are under the loading. Therefore, the researching of the routes to increase the mechanical characteristics of HA ceramics represents significant scientific and practical interest.

The initial HA powder was received by slightly modificated «wet-phase» method. A deposit was dried at 100^0 C and was pounded in the mortar then was sifted in the sieve with 100 microns size of cell. On the electron microscopy data the particles' sizes in the powder were less than 0,3 microns. Then the powder was annealed in the water steams, lifting temperature up to 800^0 C with the 100^0 C step. From these have been annealed powders were pressed (one-axis pressing) the tablets 200 mg weight, which were calcinated in the water steams at 800^0 C and were sintered at 1150^0 C during 3 hours without water steams.

The X-ray diffraction and infrared spectroscopy have shown a one-phase of the received HA ceramics within of methods sensitivity.

The research of loss in mass has shown, that the main loss of mass is fixed at temperature 400-450^0 C. These results are well correlated with the data on linear and volumetric shrinkage. It is explained by that fact, that the desorption of water and the collateral products of HA synthesis reaction is go intensive up to 450^0 C. At the annealing of the initial powder higher than 450^0 C there is not observed the significant changes. With the increasing of anneal temperature the porosity of ceramics is increased from 13 % up to 27 %, and the compressive strenght is decreased from 56 MPa (drying at 100^0 C) up to 20 MPa (annealing at 800^0 C).

On the basis of the received data there is the conclusion supposed, that the surfaces of powder particles are coated with an «amorphous» layer which consist from absorpted water, the collateral products of HA synthesis reaction and the dissolved HA; this layer is made thinner during the heating and nealy disappeared at high temperatures. However, the «amorphous» layer is promoted to significant shrinkage and, in result, much better sintering of HA samples with ceramics formation of less porosity and more compressive strenght.

HIGHLY FILLED POLYMER COMPOSITIONS BY HYDROXYAPATITE FOR ENDOPROTHETIC

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The purpose of activity - creation of biologically active polymer compositions for plastics of bones, which one bear high mechanical loads, and also for manufacturing polymer and metallic-polymeric endoprothesis. For its solution the polyurethane compositions with high containing of hydroxyapatite (HAP) were designed, which one, as is known, is inorganic component of an osteal tissue and has mitogenetic and osteotropic actions. Their physical-mechanical properties (shear strength, compression strength, strength on separation) are studied. Dynamics of an output of a medicinal preparation from the obtained compositions is studied. The model operations after a plastic of the artificially obtained defects of tibial bones of the rabbits by polymer compositions with high containing of hydroxyapatite are designed. With the purpose of analysis of processes of an activation of a bone formation the histological researches (2 weeks, 1, 3, 6, 9 months of an implantation) are conducted.

Principal components of compositions: 1. The polymer basis – oligoetherurethanediizocianate on the basis polyoxypropylenglycol (Mw=1502) and toluilendiizocianate (T65/35); 2. Bioceramics - hydroxyapatite (Ca/P=1,67, $T_{anneal.}$= 1250 °C, size of particles - 0,050 μm); 3. The immunomodulating factor – levamisole; 4. A polymerization accelerator.

The comparative analysis of physical-mechanical parameters of polyurethane compositions has shown, that the high filling by HAP a polymer basis allows essentially to increase strength of a stuff as contrasted to by control at compression - in 2,5 times, at shift - in 5,6 times that at a separation - in 3,27 times. Except for listed researches determined bond strength by polyurethane composition with hydroxyapatite of osteal tissues, which one was in 5,7 times more as contrasted to control.

The conducted model operations on experimental animal and the histological researches have shown, that highly filled by HAP polyurethane compositions are technologic enough, have high strength parameters and good adhesion, at a polymerization in a defective cavity completely replicate its form, stimulate process of an osteogenesis and can be advised for clinical tests.

BIOACTIVE CERAMICS ON THE BASIS OF CALCIUM HYDROXYAPATITE

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Traditionally various types of endoprotheses and dentures are manufactured from metals and their alloys, plastic and ceramic materials, the wide use of which is reasoned by their high mechanic properties, elasticity and the capability to undergo mechanical treatment. However, these materials have some shortcomings connected with undesirable influence on the living tissues of the organism (cancerogenic, immunologicl, bacteriologic effects). In relation with this has arisen the necessity of designing the materials that could combine high physic-chemical and mechanical properties with biological compatibility with the living tissue. Calcium hydroxyapatite (HA) belongs to such type of materials.

In this work the possibility of improvement of ceramics mechanical properties on the basis of synthetic calcium hydroxyapatite modified by the ions of lanthanum and silicon is investigated.

The precipitated from water solutions at various pH values samples containing the Ca^{2+}, La^{3+}, PO_4^{3-}, SiO_4^{4-} ions were studied by X-ray powder diffraction and IR-spectroscopy. The choice of the pH precipitation of modified HA was made on the basis of modeling of processes in initial solutions.

It has been found out that the precipitation of calcium and lanthanum phosphates with hydroxyapatite in different ratios is observed in the pH range 12,5–13,25. The pH increasing results in the change of the samples composition. The heating of these specimens at 800–1200^{0}C is accompanied by the preparation of HA modified by lanthanum and silicon ions.

The technological scheme of receiving of powders used as modifiers of HA-based compositions has been proposed.

The strength of curving of ceramics obtained from jointly precipitated powders containing Ca^{2+}, La^{3+}, PO_4^{3-} and SiO_4^{4-} ions as well as HA-based ceramics modified by these powders has been investigated.

The influence of the composition and the quantity of injected additives on the strength of ceramics samples has been studied. It has been also shown that the injection 2–7,5 wt. % of modifiers into hydroxyapatite ceramics increased the strength of curving by 2-3 times.

CONTROL OF STRUCTURE AND PROPERTIES OF BIOCERAMICS BY MEANS OF RADIO FREQUENCY SPECTROSCOPY METHODS

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With the help of electron paramagnetic resonance (EPR) and proton magnetic resonance (PMR) the properties of bioceramic materials (produced on the base of hydroxylapatite) were studied. We have developed the methods for creation of carbonateapatite and special bioceramics with paramagnetic markers, located in crystal lattice of apatite in positions of calcium, phosphorus and hydroxyl groups. Samples of bioceramics in which Ca^{2+} ions are partially replaced by ions Mn^{2+} (concentration of Mn is in limits of allowable norms) are created, thus EPR signals of Mn^{2+} ions, located in various positions of calcium, are registered separately. Paramagnetic markers allow receiving the unique information on assimilation mechanisms of implant materials in live biological object. Methods for determination of chemical affinity of implant material and biological tissue, based on EPR signal registration due to interconnected organic and mineral substances are developed. The radiospectroscopic data allow formulating the scientific grounded requirements to implant materials depending on soluble medical problems.

EPR and PMR investigations have shown, that mineral component of bone tissue represents complex composed system, which except of apatite phase contains impurity crystal phases (ICP). It is shown that ICP, despite their small quantity, play the important role in functioning of bone tissue. In bones of human and animals with the help of EPR we had investigated the phases of carbonates, oxides, tricalciumphosphate and magnetic substances, and with the help PMR the phases of nanocapillary and crystalhydrate (anisotropic) water. It is shown, that the microelements of bone tissue are located in basic not in the apatite phase, but in ICP (in particular in a calcite phase, which as a thin layer divides the apatite nanocrystals and tropocollagen molecules).

The control of technologies of bioceramics synthesis with the help of radiospectroscopy methods allows creating the new generation of composed bioceramic materials with beforehand given properties. The implanted materials made on the basis of these materials, are the most adequate to mineral component of a bone tissue. The properties such implantats, manufactured for treatment of different type of bones, are not identical and are determined by peculiarities of structure of different type bones tissue and their diseases.

MECHANICAL PROPERTIES OF MICROWAVE SINTERED Si_3N_4-CERAMICS

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The accelerated densification and lower sintering temperature are the characteristic features of the sintering in the millimeter-wave electromagnetic fields The densification velocity is exceeding both recrystallisation and grain growth velocities under millimeter-wave sintering in comparison with those under traditional heating. As a result the ceramics sintered under millimeter-wave heating have the high density and the fine grain microstructure. It would be expect that the mechanical properties of the millimeter-wave sintered ceramics will be improved.

The mechanical properties of Si_3N_4-ceramics obtained by millimeter-wave sintering (30 GHz) and under traditional heating sintering have been studied. The materials under investigation were powder blends of silicon nitride with oxides: $3\%Al_2O_3$ and $5\%Y_2O_3$ (Yb_2O_3). The specimens were sintered at 1750 ^{0}C in a nitrogen atmosphere at normal pressure, the heating rate was 60^0C/min. The relative density of specimens was 95-97%. The studied properties were Vickers hardness, fracture toughness and flexural strength. The fracture surfaces were studied by electron microscope.

It has been established that the silicon nitride ceramics with oxide additives obtained in the millimeter-wave sintering regime exhibits improved mechanical properties. Specifically, its hardness is 50 % higher and fracture toughness is 35 % higher than those of the traditionally sintered ceramics with similar relative densities. The Si_3N_4-ceramics with Y_2O_3 additive has the better characteristics. The reason for the enhanced mechanical properties is in the finer and more uniform microstructure of the millimeter-wave sintered ceramics. The average grain size for the all specimens was 0.3-0.5 μm. The results of the hardness and the fracture toughness correlate with the results the of flexure testing

ALUMINA FOR BONE SURGERY

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Today the widespread usage in bone surgery have received the alumina based ceramics which is favorable combining the hardness and wear resistance, high biocompatibility and chemical inertness, nontoxicity, high strength. Besides during long-lived stay in an organism such ceramics preserves physical and chemical properties, that provides the good premises for its reactionless ingrowing and long-lived functioning, and also makes it especially perspective for usage in bone surgery as implants.

The last years technological know-hows in the field of the ceramics as well as the powder synthesis allow to reduce noticeably impurity level in Al_2O_3 and simultaneously to increase physic-mechanical characteristics, chemical inertness, corrosion-resistance, reliability and durability of service in organism.

The alumina based ceramics for bone surgery has been developed.

The technology includes synthesis of Al_2O_3 powder with the particles size 0,3-0,4 μm with the additions of MgO and ZrO_2, which promoting densification of the ceramics and formation of homogeneous, fine grained structure; moulding and sintering of green compacts by special regime with the subsequent machining to reach given dimensional accuracy and surface quality.

The established technological route allows producing alumina based ceramic implants of any composite forms and configurations, which meet all demands in the field of biomedicine.

Main technical characteristics: chemical composition - Al_2O_3 > 99,0 %; density - > 3,92 g/cm3; the mean grain size - < 7 μm; the bending strength - 400 MPa, that meet the requirements of standards.

The dentistry implants have been developed – to create support for nonremovable tooth prosthesis, as well as ceramics cups for orthopedics hip prosthesis.

The implants have been used in clinical practice.

SOME PROPERTIES OF LOW-TEMPERATURE GLASSCERAMICS INCLUDING HYDROXYAPATITE

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There are presented experimental results of the study of glassceramics specimens sintering in two stages with temperature lower than 1100 K. As glassforming oxide are using SiO_2 and B_2O_3 with adding Na_2O.

The quantity of hydroxyapatite in composites is limited to (1-15) % mol.

According to the results of X-ray phase analisis of the investigated specimens their crystals structure correspond to the known literature date for biological hydroxyapatite (BHAp).

A porosity of glassceramics specimens and pore sizes are depended on their geometry and BHAp-contents and limited to (30-60) % vol and (3-275) mkm accordingly.

The compressive strength of those limited to (10-140) MPa if spesimens have the diameter near 15 mm and the length near 10 mm.

It was established that it is possible to change speed of dissolving of specimens in synthetic physiological solutions in interval of (0,25-5,30) % mas/day.

The mechanical strength and biosolubility of specimens made under identical conditions are dependent on the BHAp content.

The perspectives of using of manufactured glassceramics as bioactive materials in orthopady were tested «in vivo».

Class ceramics based on BHAp represent a plastic biomaterial whose physicochemical properties can be varied quite widely. It can be recommended for use in orthopedics and dentistry as a repair material in the form of blocks, granules, and cementes for repairing bone defectes.

STUDY OF HYDROXYAPATITE PHYSICAL PROPERTIES AS THE FOUNDATION FOR DIRECTIONAL CONTROL OF BIOACTIVITY

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Last time it becomes more evident that there are strong interdependence between differ ent types of defects in hydroxyapatite crystals and kinds of bioactivity which these materials display. From this point of view follows actuality of the objective of this investigation – to use the study of different physical properties to receive information on defects in synthetic HAP materials and directional control of their bioactivity.

This report includes results of measurements and discussion in terms of defects properties and their correlation with bioactivity of some HAP physical properties: electron and ion conductivity of pure and doped HAP ceramics, luminescence and adsorption.

In particular, study of HAP electroconductivity reveals prevailing ionic electrotransport which depends on HAP doping with considerable contribution of pores surface and grain boundaries, thus giving information on ways to control properties connected with mass-transport in HAP-based materials. Results of study adsorption of Ni^{2+} and Cd^{2+} ions confirm leading role of dimensional factor, which is important for ion exchange.

Study of photoluminescence spectra of stoichiometric HAP, as well as discovered for the first time thermostimulated luminescence, permits to classify the energies and kinds of electron states in HAP crystals, to find splitting of some electron states during heating, that is important to forecast chemical activity which is connected with electron exchange.

THE MAGNETIC FIELD DEPENDENCES OF RF-ABSORPTION FOR DETERMINATION OF HTS CERAMICS CRITICAL PARAMETERS

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Properties of the HTS ceramic (critical current and critical magnetic fields) are determined by the properties both HTS grains and intergranular contacts which can be changed in a wide range varying conditions of the samples synthesis. Practical application of these ceramics, for example, in magnetic screens, sensors of electromagnetic radiation, electric engines, *etc.* depends on properties of these materials.

The analysis of the magnetic - field dependences of RF-absorption can be used as effective and nondestructive method of the sample quality determination.

A lot of $YBa_2Cu_3O_{7-x}$ ceramic samples which were prepared according to solid-state reaction technique with variations of pressure, temperature of annealing, doping with Ag, application of additional heating in the course of synthesis, as well water degradation were investigated. Using the inductive technique three kinds of the magnetic field dependences of rf-absorption at the same time for each specimen were measured: the dependences in increasing, decreasing and residual magnetic fields, and also the same dependences in the case of inverting the sign of the magnetic field.

It was shown, that this technique allows to determine characteristics of both grains and intergranular medium, such as magnitude of magnetic field penetration into the sample through a network of Josephson junctions between grains, first critical fields for grains and intergranular medium, and quality of the grains contacts as well. It was established that increasing of pressing strength in process of the samples fabrication causes improvement in superconducting properties of intergranular contacts. The additonal heating at the peritectic temperature overstepping influences on quality of both intergranular weak links and grains. The addition of silver leads to the weaking intergranular contacts. When contacting with water, first of all a network of Josephson junctions is destroyed. But it can be restored by additional sintering.

MASS SPECTROMETRY AS A COMPLEMENTARY METHOD TO THERMAL ANALYSIS (DTA/TG) IN CHARACTERIZATION OF CERAMIC MATERIALS

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Thermal analysis is one of the most important methods of detection of some exo- and endothermal processes taking place during heating of material. Chemical reaction is often connected with change of mass of reacting system. If we are interested in reaction mechanism, in nature of occurring processes, the knowledge concerning qualitative and quantitative composition of evolving gas is required. One of the methods of determination of gaseous mixture composition (EGA) is mass spectrometry, which permits to specify molar mass of components. DTA/TG apparatus connected on-line with mass spectrometer (DTA/TG/EGA system) is a powerful tool for determination of solid → solid + gas reaction mechanism. As an example Fig.1 illustrates the results of simultaneous DTA/TG/EGA analysis during thermal decomposition of $Cr(NO_3)_3 \cdot 9H_2O$. This reaction is used for Cr_2O_3 powder production. Even without detailed analysis of these results, we can see that N_2O, NO and NO_2 are observed in gaseous products of decomposition. It is also evident that after nitrate decomposition some CrO_x with $x>1.5$ is formed. Thus Cr_2O_3 ($CrO_{1.5}$) is not a product of chromium(III) nitrate(V) decomposition, but is formed by thermal decomposition of $CrO_{x>1.5}$ at temperature higher than 400°C. Simultaneously, this result can be considered as a proof that reduction N^{5+} to N^{+}, N^{2+} and N^{4+} proceeds by oxidation Cr^{3+} to Cr^{m+} where m is equal to 4 or 6.

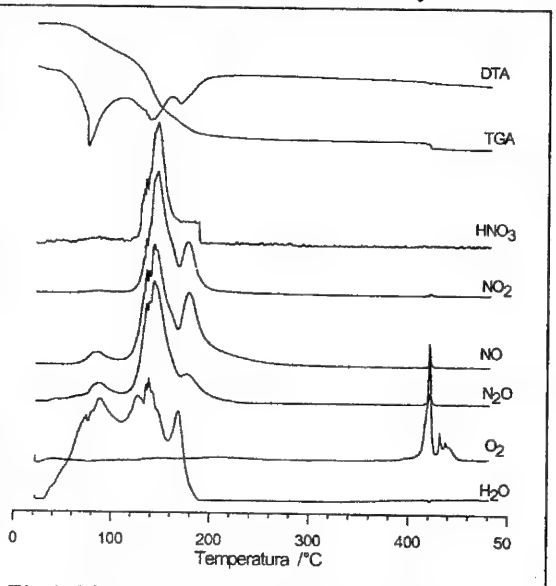

Fig.1. Thermal decomposion of $Cr(NO_3)_3 \cdot 9H_2O$

TETRAGONAL ZIRCONIA POLYCRYSTALS IN THE $CaO–Y_2O_3–ZrO_2$ SYSTEM

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Co-precipitation technique is an useful way of preparation of multicomponent ceramic powders in the case of oxides containing cations not very distant in the periodical table of elements. From this point of view preparation of the materials in the $Y_2O_3–ZrO_2$ system is an easy task. But quantitative introduction of CaO into this binary system makes some troubles. The problem was solved by application as a precipitation agent a mixture of ammonia and ammonium carbonate solution. It was found that the coprecipitated gel in the $CaO–Y_2O_3–ZrO_2$ system contained no calcium carbonate. Its low temperature calcination resulted in the crystallisation of the triple solid solution. The results of a systematic study on the effect of chemical composition of the sintered materials in this system on their phase composition, hardness, elastic properties and fracture toughness will be shown.

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MECHANICAL PROPERTIES AND CRYSTALLOGRAPHIC ORIENTATION CHARACTERISATICS OF SELECTED PARTICULATE COMPOSITES

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The paper presents results of investigations on mechanical propertis characterisation of particulate composites. As a matrix solid solution of 3 mole % of yttria in zirconia was used. Hard carbide particles were incorporated into the matrix - tungsten carbide (WC), niobium carbide (NbC), tantalum carbide (TaC), hafnium carbide (HfC) and zirconium carbide (ZrC). Composite powders containing 20 vol. % of carbides were hot-pressed at 1500°C. Densities of sintered bodies ranged from 96 to 99 % of theoretical values. Elastic properties of composities were determined by the ultrasonic method. Three-point bending test allowed to estimate the bending strenght of materials. The indentation method was used to determination of Vickers hardness and fracture taughness. The transmission electron microscopy investigations detected the presence of crystallographic correlations between zirconia and selected carbide phases. The scanning electron microscopy combined with electron backscaterred diffraction (EBSD) method allowed to obtain maps of crystallographic orientation of single grains in the composite materials.

It was established that carbides of similar physical and chemical properties influence in a different way the composite mechanical properties. Incorporation to the zirconia matrix of tungsten, niobium and tantalum carbides improved mechanical properties of the material. Composites with hafnium and zirconia carbides did not reveal mechanical properties improvement. The EBSD measurements showed that in the case of composites with better mechanical properties it was possible to establish crystallographic correlations between carbide and oxide grains. In the case of composites with zirconium and hafnium carbide additives no such relationship were found.

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PHYSICAL AND MECHANICAL PROPERTIES TESTING OF TECHNICAL CERAMICS BY NATURAL OSCILLATION FREQUENCIES OF PRODUCTS

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Natural oscillation frequencies of products depend on elastic constants which are connected with such physical and mechanical properties of ceramic materials as hardness, strength, resistance to impact, wear resistance, porosity, density and etc. The elastic constants of ceramic material are connected both with composition, structure and conditions of manufacturing of products and with their operational properties.

Non destructive testing method based on measuring of natural oscillation frequencies of products takes precedence over another acoustic testing, for example ultrasonic, because allows to test products with surface roughness and open porosity, small-size products.

Nowadays the latest version of "Zvuk" series of equipment for measuring of natural oscillation frequencies is carried out. The devices "Zvuk-110M" and "Zvuk-203M" are computer controlled systems that use special software, allowing measurements to be made automatically.

The devices "Zvuk" allow to determine elastic constants of products of such forms as bars, cylinders, disks and square plates, and also products of other forms and various sizes. For bars and cylinders elastic constants determination according to the American standard C 1259-94 "Standard Test Method for Dynamic Young's Modulus, Shear Modulus and Poisson's Ratio for Advanced Ceramics by Impulse Excitation of Vibration" (Annual Book of ASTM Standards, Vol. 15.02) is acceptable. Testing products of another forms is carried out by using original software.

The device "Zvuk-110M" consists of special electronic circuit board built-in into IBM compatible computer and measuring rack with piezoelectric transducers. The special software for the device enables the frequency analysis of a spectrum and the identification of the natural modes of vibrations. The device "Zvuk- 203M" protected by the patent of Russia is a portable hand held device, which has a built-in microphone and liquid crystal display. The outcome is in the form of either the natural frequency of the test sample or a characteristic connected to this frequency, for example, sound velocity, Young's modulus and etc. Since the change of natural frequencies of samples can be caused by defects, the device may be used for rapid production quality control and easily incorporated in production lines.

EXAMINATION OF CERAMICAL MATERIALS FOR FERROUS INCLUSIONS CONTENT

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Products are used in producing of technical, structural, refractory, building, electro and radio ceramics contain ferrous inclusions. The inclusions can't be extracted at the beginning of producing, both this and high temperature of technological processes degrade the technical and operating characteristics of ceramics. That's why it is necessary to make operating and quite exact control of mentioned contents during the different stages of production.

Electromagnetic measurement method and electronic devices with inductive transducers meet these requirements to the highest degree. The basis of the method relationship between magnetic permeability of the tested assay and content of metallic inclusions.

"NPK "Abrasives & Grinding" has elaborated and producing for several years the device "Magnit – 704", which is designed to control ferromagnetic inclusions in range from 0% to 3.0%, the instrumental inaccuracy doesn't exceed ±4%, resolution capability 0,0001% on the most sensitive sub-ranges (0% - 0,01%). Measurement time of one assay doesn't exceed 10 seconds.

The device is certificated (certificate RU.C.34.022.A № 8815) and included to the State Catalogue of means of measurement. The state standard samples - simulators, designed and made by our firm, of a mass lobe of a magnetic material in grinding stuffs is the basis of metrology maintenance of the device (certificate № 1278, number in the State Catalogue is 3257-85).

The device is widely used in all firms-producers of abrasive grinding materials and tools. The device can be also used to control the quality of vitrify bonds for producing abrasive tools, of slip in production of electro-technical porcelain articles, of materials for producing radio-technical ceramics, of high-porous structural ceramics. The experience shows possibility of using device "Magnit-704" in various brunches of industry, connected with producing and using of ceramic materials.

NUMERICAL MODELLING OF PERIODICAL CHANGES OF CERAMIC MASS RHEOMECHANICAL BEHAVIOUR

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The process of ceramic moulding depends on peculiarities of particle interactions in pastes, suspension, etc. Pastes and suspensions widely used in ceramics have high viscosity, which complicates moulding of mass. The rheological properties of ceramic mass depend on interparticle and collective interactions, which are defined by distribution of bonds and dynamics of their destruction and restoration. In highly concentrated disperse systems the particle's coordination number is high, so, structuring phenomena and thixotropy are usually observed for these systems. The gel structure can change with time for a given shear rate in a case when the rates of bond destruction and rebuilding are non-balanced and it recoils upon suspension viscosity. In the balanced regime, the periodical changes of rheological properties can be observed at equilibrium between the rates of bonds destruction and rebuilding. The equilibrium position in thixotropic systems can be regulated by electrolytes, polymeric additives, etc

In our work we simulate the structure of a thixotropic suspension with a simple model of mechanical networks. In this model, the bonds can get destructed and rebuilt with the lapse of time. A bond gets destructed at some critical load. The rebuilding process is characterized by a time constant τ. Dependencies of the system destruction degree P versus time t at periodical changes of external stress and at different amplitude, frequency and τ values were calculated. In the numerical model the stable periodical changes of system destruction degree P with time t were observed. The simulation results were compared with experimental data for periodical changes of viscosity in various thixotropic suspensions of montmorillonite, silica and cement. The present study proposes a new correlation for shear-rate-dependent effective viscosity of clays and silica suspensions. The obtained results can be used for control of the physico-chemical properties of ceramic mass.

INFLUENCE OF POST-SINTERING STRESSES ON BRITTLE FRACTURE OF CERAMICS

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Increased fracture toughness of ceramics determines its broader application as a structural material. The known toughening methods are based on mechanisms capable to relax stresses concentrated at the crack tip. In most cases this effect is achieved by provoking crack deflection or by consuming strain energy by a phase transformation. Crack deflection occurs when the crack front advancing through the material meets an inclusion of other phase or meets an area of local stresses. These stresses can be created by incorporating in a matrix material particles of inclusions characterised by lower coefficient of thermal expansion than the matrix.

A study on the effect of stresses on fracture toughness were performed using three pseudo-binary systems differing in the way of fracture of the matrix material. Silicon carbide, aluminium nitride and titanium silicon carbide (Ti_3SiC_2) were applied as the matrices. Transgranular fracture is characteristic for SiC. In the case of AlN intergranular fractures occur. Complex way of fracture is observed in Ti_3SiC_2. Results of experiments confirm the assumptions on which this study is based and prove that this is an effective way of increasing fracture toughness of brittle ceramics.

COMPUTER-AIDED MODELING OF IMPACT INTERACTION OF STEEL STRIKERS WITH MULTILAYER BARRIERS BASED ON STRUCTURAL CERAMICS

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At present behavior of ceramics-based shock-resistant barriers at impact rates close to the ballistic limitis still poorly understood. At above impact rates when inertia forces are comparable to the parameters of the barrier material static strength, and the barrier is distroyed due to propagation of cracks with possible subsequent penetration of a striker into already destroyed material, the existing calculation methods, as a rule, have a limited application.

In this connection, we have developed a new engineering approach based on computer-aided modeling of a high-rate interaction of strikers and a barrier being deformed at the initial instant of impact. The approach consists of the following stages:

- evaluation of the impact force and the distribution of contact pressure over the shock-resistant barrier surface with due account of large plastic deformations of a steel striker as wellas the peculiarities of its contact interaction with a barrier;
- finite-element modeling of stressed-strained and limiting states of a shock-resistant barrier at different impact angles and rates including those close to the ballistic limit;
- determination of the ballistic limit (minimum striker velocity, at which the target breaking-through is still possible) based on calculation of reduced radius and mass of a part of the shock-resistant barrier "involved" into the impact.

It was found that in case of a normal impact ($\alpha=0$), the value of radius R of a target "involved" into the impact is determined as a border, outside which axial stresses $\sigma_y < 10\% \max\sigma_y$. As a criterion for the determination of R for impact angles $\alpha\neq0$, we took the radius of the pressure center (adjacent to the impact zone) the size of which is determined on the basis of distribution of maximum principal stresses σ_1. Through comparison of stress fields σ_y and σ_1 for normal impact, we calculated the $\sigma_1/\max\sigma_y$ ratio that determined the pressure center border for all impact angles α.

With the use of this approach, we have solved the problem of optimization of the composition and the geometrical parameters of a three-layer shock-resistant barrier based on a ceramic plate of silicon carbide. We have found the optimum ratio of thicknesses of layers of kevlar on the face and back sides of the ceramic plate enabling one to exclude, at a limited thickness of the entire combined armored package, its breaking-through with a steel striker with kinetic energy of up to 3,5 kJ.

TESTING OF THIN FILM TECHNOLOGY FOR PRODUCING FUNCTIONAL CERAMICS AND GLASS

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Development of material science in the field of microelectronics and miniaturization of optoelectronic systems is connected with modernization of the thin film technology. One of the directions is application of superthin films produced by Lengmur-Blodghet (LB) method. However, production of luminescent, dielectric , semi-conductive and other LB films has a number of difficulties connected with the necessity to test a number of parameters responsible for spectrum-luminescent , dielectric and other service properties of thin film materials.

The developed methods of testing are based on ellipsometric which determines changes in polarization of a monochromatic light beam resulted from its interaction with the film (sample) studied depending on its composition and structure. These changes are measured by means of polarization angles Δ and ψ connected with a value of relative reflection factor via the basic equation of ellipsometric:

$P = \frac{R_p}{R_s} = tg\psi e^{i}$, where P is the reflection factor, Rp and Rs are Frenel coefficients

The accuracy of determination of ellipsometric angles depending on errors of cos Δ and tg ψ determination increases the accuracy of calculation by an order as compared to Shelybskyi method which is used only for testing of glass probe, with a particle size of no less than 2 mm.. Unlike the known methods the elipsometric provides making accurate determination of water amount in films without their failure and determining thickness of these films up to values 3 Å.

The application of the technique developed provides increasing efficiency and accuracy for determining spectrum-optical properties , structure uniformity, thickness of films and water amount in them, as well as gives an opportunity to determine directly the mentioned properties in thin films and articles without their failure.

THE PHASES EQUILIBRIUM OF A QUASIBINARY W_2B_5 -B_4C SYSTEM

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Cause refractory of metals borides and carbides majority state diagram with their participation are investigated insufficiently full. But as these data are necessary for creation of new materials and coverings proof in various aggressive surrounds (liquid metals and alloys, oxygen and etc.) and in this connection demaind further investigate the state diagram of this type systems.

Phase equlibruim in system W-B-C investigated in a number of issues. An isothermal section of this system at T = 1973 K is investigated by a XRD analysis[1]. Ternary compouds in system W-B-C arent discovery. Threefold connections in systems of W - B - C it is not revealed, but as given in the field of existence of liquid alloys are not known, is of special interest to investigate a number quasibinary systems, containing of metals borides and carbides. In this connection phase equlibruim of system W_2B_5 - B_4C was investigated

Samples of alloys were received by sintering of powders of the mark pure (size of particles ≈ 2-5 nm) method of hot pressing in the graphite press-cell. Homogenization of samples carried out at 2300 K during two hours. The temperatures of a melts beginning and crystallization of alloys defined by a Pirani-Altertum method and high-temperature differential-thermal analysis. Structure of pressed and homogenized alloys was investigated by XRD and optical metallography analysis.

It has been established, that the investigated alloys form the eutectic type of state diagrams. Eutectic is necessary on composition of 55 mol % of W_2B_5 and having melting point 2370 K.

As the researches phase equilibrium in systems containing carbides and borides of metals are very labor-consuming and I demand highly of temperature equipment, it is expedient to apply settlement methods to these purposes. We have applied a thermodynamic method to forecasting the diagrams of a condition of a number quasibinary of systems. The initial data for pure components were taken from the references, and some are designed under the additive law. Thermodynamical properties of a number quasibinary of systems in liquid state calculated from dates for ternary systems of W -B - C received on equation of Tupa as most appropriate. The parameters of stability of phases are determined on the basis of an experimental research described above. Has appeared, that the state diagrams of designed quasibinary systems containing W_2B_5, TiB_2, B_4C and other refractory compounds are correlate with. experimental investigated and well-known from literatures.

ABLATION CONTROL OF QUARTZ HEAT-PROTECTING MATERIALS BY MEANS OF IHGTGUIDES

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Due to the application of the technology for ceramic dross casting quartz glass is used for manufacturing heads of descent spacecrafts, antenna caps and leading edges and also cellular details reinforced with stainless steel and other articles.

The control of operating characteristics of such articles and the ablation of quartz heat-protecting materials in particular is of considerable practical interest. In the IPMS NASU the light guide sensors of ablation and the method for their installation into quarts heat-reflecting materials during their manufacturing by the technology of ceramic dross casting have been developed.

As the results of mechanical tests have shown the recilience of the articles increases 1,6 times when the number of the light guides in the sample cross-section changes from 0 to 5. The elastic modulus value (3580-3730 kg/mm^2) remains on the level of non-reinforced ceramics. The safety factor of the article with sensors is within the limits of 1,22-1,26. It corresponds to the safety factor of full-scale cap. The dielectric properties of quartz ceramics reinforced by light-quides by room temperature correspond to the values for non-reinforced one. When the temperature increases up to 1473 K the value of permittivity increases from 3,34 up to 3,54 and the tangent of dielectric loss angle increases from 5 to 105.

The results of X-ray control are indicative of the absence of the defects in the structure of cap material and its solidity.

The experimental data concerning the standard cape ablation data have been obtained with the help of light guides sensors under the following conditions of air braking:

$$P_e = 11 \text{ MPa}, \quad q = 4{,}2 \bullet 10^4 \text{ kW/m}^2, \quad T_e = 3100 \text{ K}.$$

The obtained data are coordinated well with the results of filming. The light guides do not influence upon the destruction of quartz ceramics.

THERMAL STRENGTH RESEARCH OF REFRACTORY COMPOUNDS IN ALLOYS ON BASIS OF SYSTEM $Me^{IV}C$-$Me^{IV}B_2$

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One of the most important characteristics of refractory metallic compounds is creep resistance, which is determined by diffusion controlled process. The most reliable information about regularities in change of creep speed is collected mainly for specific carbides and borides of titanium and zirconium. It was shown that basic factors which influence this value are grain size, stochiometric composition and temperature. Importance of non-threshold creeping of refractory compounds is great, since working temperature of such materials reaches 0,5 - 0,6 of melting temperature [1,2]. It was less studied composite alloys, specifically systems of $Me^{IV}C$-$Me^{IV}B_2$,where Me is d – element of IV group of periodic table. In the presented work there have been generalized the research results of creeping of heterogeneous fine-dyspersated phases in systems $Me^{IV}C$-$Me^{IV}B_2$, which are especially interesting from angle of secondary display of "structural superplasticity's" effect, which is typical for two-phase materials. The testing specimens have been made according to well-known ceramic technologies, formulation of original components was in accord with definite stehiometry. Synthesis of original components was made according to techniques [3]. Testing was carried out under conditions of helium medium in temperature range of 1700-2420°C and compression was varied from 5 to 30 MPa during 30-60 min. It was carried out an experimental work and were obtained dependence data of creep speed from T и σ. Activation energy of creeping calculated for two-phase alloys was 70kcal/mol.

For systems TiC – TiB_2 research results of dependence from compression has been shown nonlinearity in the whole studied temperature range. Activation energy was calculated on the basis of dependence of creep speed from temperature and was 95-110 kcal/mol under $\sigma_{compression}$ from 5 to 10 MPa respectively. Absence of dimensional change of the grains under attainment of maximal deformation indicates that the basic contribution in overall deformation is made by sliding motion on interphase boundaries. The experimental data for investigated alloys have indicated that maximal deformation and its speed are observed in compositions with volume proportion of carbide and boride phases 1:1, that is reflection of highly developed interphase boundaries of the grains.

MICROMECHANICAL CHARACTERISTIC OF RARE EARTH DODECABORIDES METALS

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Rare Earth Dodecaborides metals present itself perspective a class of refractory compounds, with dominating covalente relationships B-B. Mechanical, firmnessate characteristic of these phases practically not explored.

In work on samples an dodecaborides YB_{12}, ZrB_{12}, TbB_{12}, HoB_{12}, DyB_{12}, MoB_{12}, ErB_{12}, LuB_{12} tinned by the method by the borothermal reduction of the oxides corresponding metals by the boron in the vacuum and hurried in backfilling of the same name powder in the ambience of argon explored microhardness on microhardnessmetr ПМТ-3.

From tin results follows that microhardness dodecaborides greatly depends on loads on identor. As from certain value (for dodecaborides 100 g) value microhardness becomes practically independent from the load. Calculated values microhardness for dodecaborides above than beside Rare Earth metals and bora and are 3200, 3000, 2600, 2700, 2800, 3000, 2900 kg/mm2 accordingly, for YB12, ZrB_{12}, TbB_{12}, DyB_{12}, HoB_{12}, TmB_{12}, ErB_{12}, LuB_{12}.

Using work Oshcerina B.N. for semiconductors and carbides with the structure of type NaCl is made attempt to value on the base microhardness dodecaborides (crystalline structure too NaCl) their three-dementional modulas of compressibility (Ks) and specific free shallow energies of crystals ($\delta_{(hkl)}$).

Tinned such results:

Three-dementional module of compressibility Ks – $1{,}24*10^{12}$; $1{,}17*10^{12}$; $1{,}00*10^{12}$; $0{,}92*10^{12}$; $1{,}04*10^{12}$; $1{,}08*10^{12}$; $1{,}16*10^{12}$; $1{,}12*10^{12}$ N/m^2 accordingly, specific free shallow energy of crystals $\delta_{(100)}$ – 12,22; 11,45; 9,92; 9,15; 10,30; 10,68; 11,45; 11,07 Dg/m^2 In the same order.

MICROTRIBOTEST FOR STUDIES OF CONTACT INTERACTION OF PAIR FRICTION

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Microtribotest is intended for the friction features studies of friction materials and their separated structure components.

Microtribotest is computerized and had program package, which allow to analyse in situ load friction, friction coefficient, triboEMF, conductivity or voltage falls on the contacts.

Microtribotest technical features:

* Load, g	from 5 to 200
* Scan rate, mm/min	from 0,2 to 10
* TriboEMF, μV	from 1
* Voltage falls, μV	from 0,1 to 100

THE USE OF ACOUSTIC METHODS FOR THE QUALITY CHECKING AND TESTING CERAMIC MATERIALS

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Ceramic materials (CM) have a wide set of structural states and a spectrum of phase components properties that allows to produce materials with unique physical and mechanical characteristics (PMC) for various applications. Resulting properties of CM are determined by not only properties of initial components, but to a considerable extent by the production technology which integral part is the check of a production quality and physical and mechanical properties. Taking into account peculiarities of a CM composition, not all the physical methods which are used for metals may be used to check and test CM. Acoustic methods should be marked out as long-range.

Acoustic methods are widely used for non-destructive inspection, measurement of thickness and elastic characteristics for CM. The use of those methods for more fine structural investigations are still limited. Possibility of using any indirect non-destructive method including acoustic one for checking and testing materials is conditioned by availability of a correction connection between the investigated material property and the measured characteristic of a physical field. In terms of above mentioned it is interesting to determine relationships between structure sensitive characteristics of elastic waves (EW), such as an attenuation coefficient and a propagation rate, on the one hand, and structural parameters and PMC of CM, on the other hand.

To determine the connection between EW characteristics of sintered ceramic composites and parameters of their structure and physical properties the structural models were chosen for the material as heterophase systems in which elements of each phase have the simplest geometrical form and are uniformly distributed within the bulk material. Analysis of the acoustic field was performed within the scope of the elasticity theory for a solid with a low porosity (no more than 20%). The mathematical connection between EW characteristics and coefficients of elasticity for CM, their phases concentration and elements sizes for those phases was revealed. Calculated relationships were compared with empirical ones studied during measuring propagation rates and attenuation coefficients of EW in CM based on silicon nitrid, aluminium oxide, diamond-based composites. Analysis of possible causes of deviation in empirical relationships from calculated ones was performed. It was shown that by measuring propagation rates for EW one could perform testing CM elasticity characteristics, judge about phases concentration in CM and check the presence of defects in the structure; by measuring attenuation coefficients one could judge about phases concentration in CM, elements sizes of those phases and check the presence of defects in the structure.

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